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(54) Title: ARYL-ARYL DENDRIMERS

G2-Zn-Porphyrin Dendrimer

1
G2-CHO

11
G2-Zn-Porphyrin
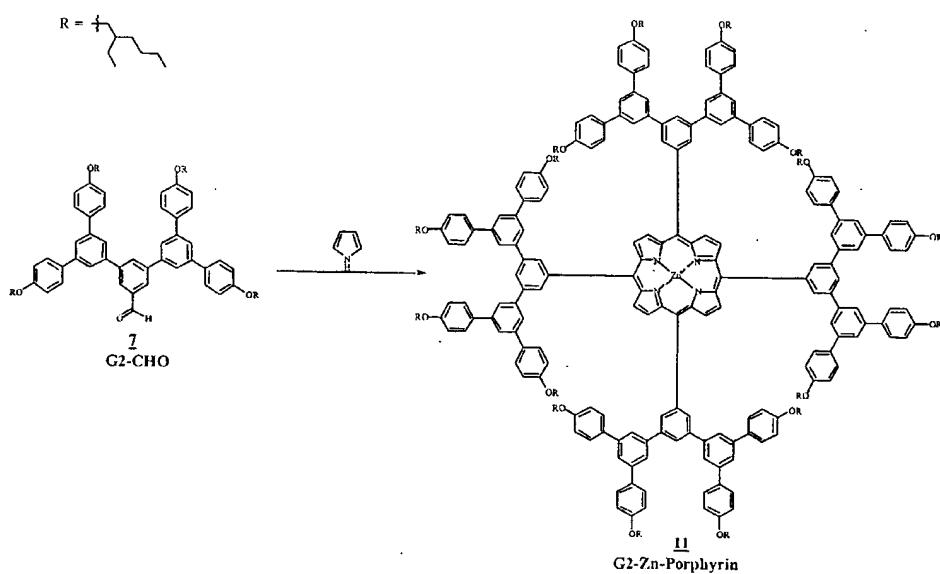
(57) **Abstract:** Light emitting devices are described which incorporate, as the light emitting element, a dendrimer of which the constituent dendrons include a conjugated dendritic structure comprising aryl and/or heteroaryl groups connected to each other via bonds between Sp² hybridised ring atoms of said aryl or heteroaryl groups.

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ARYL-ARYL DENDRIMERS

This invention relates to dendrimers and light emitting devices containing them.

5   Light-emitting materials fall into three classes, namely molecular, polymeric, and dendritic. Dendritic materials have several advantages over molecular and polymeric materials including: a) the electronic properties can be changed without altering the processing properties; b) a greater variety of chromophores can be used as the dendritic architecture can stop π-π stacking of the chromophores; c) the

10   efficiency of light-emitting diodes can be controlled by the dendrimer generation i.e. the number of sets of branching points within a dendron; and d) the dendrimer architecture makes the formation of blends with other dendrimers, polymers and molecular materials simple. Dendrimers consist of dendrons or dendritic structures terminating in surface groups and a core (see Figure 1). Dendrons also known as

15   dendrites have at least one, and preferably more than one, branching point. The branching points are atoms or groups to which at least two branches or linkers are attached. The nature of the branching points and the links between the branching points can be varied. A branching group is generally connected to the next branching group optionally via one or more linking groups (eg aryl - aryl' - aryl) where aryl is a

20   branching group and aryl' a linking group. There are at least three attachments in total to a branching group, but only two are necessary to a linker group.

There have been a number of classes of light-emitting dendrimers reported with the main differences observed in the dendron architecture. The first report of a light-emitting dendrimer had a fluorescent core and phenylacetylene based dendrons.

25   More recently a superior system has been reported where the dendrimers are again comprised of a fluorescent core but the dendrons contain stilbene moieties. Dendrimers based on this latter architecture have been shown to have the advantages described above over molecular and polymeric materials. Some simple dendrimers that contain biphenyl based dendrons have also been described. Finally, there have

30   been a few reports of dendrimers that contain luminescent chromophores but where the dendrons contain non-conjugated branching points. These latter materials have

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the potential disadvantage that much of it is comprised of electrically insulating

groups. The dendrimer types that are likely to have the greatest promise are those

that contain mostly conjugated dendrons. These include those described in

WO99/21935. However, aryl-vinyl-aryl dendrons may not be optimal for

5   electroluminescent devices. For example, in polyarylenevinylene based light

emitting devices, the vinyl groups have been implicated as degradation sites. By

analogy the vinyl groups in aryl-vinyl-aryl dendrons may be potential degradation

sites. It may therefore be desirable to avoid vinyl groups. Also the control of colour

and charge transport in dendrimers is governed by the interactions between

10   dendrimers and is changed by altering the shape and generation of the dendrimer.

Aryl-aryl'-aryl dendrons will be a different shape to aryl-vinyl-aryl dendrons.

According to the present invention there is provided a light emitting device

(i.e. visible light) containing a dendrimer in which the dendritic structures comprise

branching, and optionally linking, (hetero) aryl groups wherein each aryl group is

15   directly attached to another (hetero) aryl group. Thus the dendritic structure is aryl-

aryl or aryl- (aryl')$_a$-aryl (where aryl' may be different from aryl and a is integer from

0 to 4).

Thus in the at least inherently partially conjugated dendrimers of this

invention the core terminates at the single bond to the first branching group, i.e. a

20   bond to the sp^2 hybridised ring atom of a (hetero)aryl branching group, the ring atom

forming part of the dendron. Typically the ring atom will be carbon.

The present invention provides, in particular, a light-emitting device

incorporating as its light emitting element a compound having the formula (I):

CORE-[DENDRITE(-Q)$_a$]$_n$ (I)

25   in which the CORE represents an atom or group, n represents an integer of at least 1,

Q is a proton or a surface group, a is an integer and DENDRITE, which may be the

same or different if n is greater than 1, represents a conjugated dendritic structure

comprising aryl and/or heteroaryl groups connected to each other via bonds between

sp^2 hybridised ring atoms of said aryl or heteroaryl groups, CORE terminating in the

30   first single bond which is connected to an sp^2 hybridised ring atom of an (hetero)aryl

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group to which more than one conjugated dendritic branch is attached, said atom

forming part of the DENDRITE, the CORE and/or DENDRITE being luminescent;

provided that the compound is not :
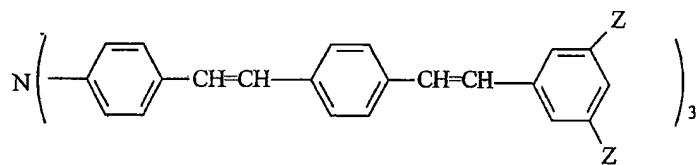
5   wherein each Z is a group of formula:
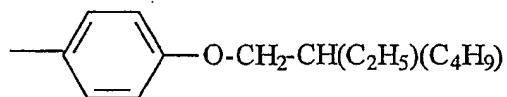
In another aspect the invention provides a light emitting device incorporating

as its light emitting element a compound having the formula (II):

$$CORE\text{-}[DENTRITE(\text{-}Q)_a]_n \quad (II)$$

10   in which the CORE represents an atom or group other than a nitrogen atom or a

group of tetrahedral shape, n represents an integer of at least 1, Q is a proton or a

surface group, a is an integer and DENDRITE, which may be the same or different if

n is greater than 1, represents a conjugated dendritic structure comprising aryl and/or

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heteroaryl groups connected to each other via bonds between sp^2 hybridised ring

atoms of said aryl or heteroaryl groups, CORE terminating in the first single bond

which is connection to an sp^2 hybridised ring atom of an (hetero) aryl group to which

more than one conjugated dendritic branch is attached, said atom forming part of the

5   DENDRITE, the CORE and/or DENDRITE being luminescent.

In each structural unit [DENDRITE$(-Q)_a$] of formula (I) or (II) as defined

above, a is 0 or an integer which equals the number of bonding atoms of the distal

end groups of DENDRITE which are not attached to a branch point. The parameter a

increases with increasing generation. For example, in a DENDRITE which consists

10   of two distal phenyl rings, a is 10. In a higher generation, where the DENDRITE

consists of 4 distal phenyl rings, a is 20. In a preferred embodiment at least one

bonding atom on each distal group is attached to a Q which is not a proton.

In this context, conjugated dendrons (dendrites) indicate that they are made

up of alternating double and single bonds, apart from the surface groups. However,

15   this does not mean that the π system is fully delocalised. The delocalisation of the π

system is dependent on the regiochemistry of the attachments.

Thus the dendrimers contain at least one aryl-aryl or, more generally, aryl-

$(aryl')_a$-aryl group, wherein aryl includes heteroaryl and aryl' is the same as or

different from aryl and a is an integer from 0 to 4. It is to be understood that

20   references to aryl (and aryl') include heteroaryl and fused aromatic ring systems.

It is also to be understood that not all the aryl groups are necessarily

branching groups e.g. as in
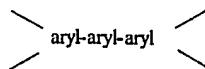
where the central group is a linking group.

25   In one embodiment the structure is not ⟍phenyl-phenyl⟋.

Thus it is preferred that when phenyl is the branching group then the structure

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of the dendron contains ⟍phenyl-other aryl⟋, ⟍phenyl-phenyl- phenyl⟋or ⟍phenyl-
other aryl-phenyl⟋.

In addition, one dendron can contain more than one type of link between the
branch points or different branch points. For example, a single dendron may contain
a mixture of phenyl-phenyl branches and, say, phenyl-pyridyl branches.

The dendrimer may have more than one luminescent moiety and the energy
resulting from electrical or optical excitation may be transferred to one of them for
light emission. In a preferred embodiment the dendrimer incorporates at least two
inherently at-least-partly-conjugated luminescent moieties which moieties may or
may not be conjugated with each other, wherein the dendron includes at least one of
the said luminescent moieties. Preferably the luminescent moiety or moieties further
from the core of the dendrimer have a larger HOMO-LUMO energy gap than the
luminescent moiety or moieties closer to or partly or wholly within the core of the
dendrimer. In another embodiment the HOMO-LUMO energy gap is substantially
the same although the surface groups may change the HOMO-LUMO energy gap of
the chromophores at the surface of the dendrimer. Sometimes in, say, the second
generation dendrimer the surface group makes the chromophore at the distal end of
the dendrite of lower HOMO-LUMO energy compared to that of the next one in.

The relative HOMO-LUMO energy gaps of the moieties can be measured by
methods known *per se* using a UV-visible spectrophotometer. The graduation of
HOMO-LUMO energy gap being lower in those luminescent moieties which are
closer to the core may be generally beneficial in encouraging inwards charge transfer
and increased light-emitting activity within the dendrimer molecules. One of the
luminescent moieties may be, or (partly or wholly) within, the core itself, which will
thus preferably have a smaller inherent HOMO-LUMO energy gap than the other
luminescent moiety or moieties in the dendron. Alternatively, or in addition, the
dendrons themselves may each contain more than one luminescent moiety, in which
case those further from the core will again preferably have larger inherent HOMO-

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LUMO energy gap than those closer to the core. In this case, the core itself need not be luminescent, although luminescent cores are generally preferred.

Suitable surface groups for the dendrimers include branched and unbranched alkyl, especially t-butyl, branched and unbranched alkoxy, such as 2-ethylhexyloxy

5   or n-butyloxy, hydroxy, alkylsilane, carboxy, carbalkoxy, and vinyl. A more comprehensive list include a further-reactable alkene, (meth)acrylate, sulphur-containing, or silicon-containing group; sulphonyl group; polyether group; C_1 to C_{15} alkyl (preferably t-butyl) group; amine group; mono-, di- or tri-C_1 to C_{15} alkyl amine group; -COOR group wherein R is hydrogen or C_1 to C_{15} alkyl; -OR group wherein

10   R is hydrogen, aryl, or C_1 to C_{15} alkyl or alkenyl; -O_2SR group wherein R is C_1 to C_{15} alkyl or alkenyl; -SR group wherein R is aryl, or C_1 to C_{15} alkyl or alkenyl; -SiR_3 group wherein the R groups are the same or different and are hydrogen, C_1 to C_{15} alkyl or alkenyl, or -SR' group (R' is aryl or C_1 to C_{15} alkyl or alkenyl), aryl, or heteroaryl. Typically *t*-butyl and alkoxy groups are used. Different surface groups

15   may be present on different dendrons.

It is preferred that the dendrimer is solution-processable i.e. the surface groups are such that the dendrimer can be dissolved in a solvent. In one embodiment the surface group is such that, on processing, the dendrimer can be photopatterned. For example a cross-linkable group is present which can be cross-linked upon

20   irradiation or by chemical reaction. Alternatively the surface group comprises a protecting group which can be removed to leave a group which can be cross-linked. In general, the surface groups are selected so the dendrimers are soluble in solvents suitable for solution processing.

The aryl (and aryl') groups within the dendrons can be typically benzene,

25   napthalene, anthracene, fluorene, pyridine, oxadiazole, triazole, triazine, thiophene and where appropriate substituted variations. These groups may optionally be substituted, typically by C_1 to C_{15} alkyl or alkoxy groups. The aryl groups at the branching points are preferably benzene rings, preferably coupled at ring positions 1, 3 and 5, pyridyl or triazinyl rings. The dendrons themselves can contain a, or the,

30   fluorescent chromophore.

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The cores can be comprised of luminescent or non-luminescent moieties. In the latter case the dendrons must contain fluorescent groups. In the case of the cores being luminescent they can be comprised of either organic and/or organometallic fluorophores and/or phosphors. Typical cores include one or more moieties of

5   benzene, pyridine, pyrimidine, triazine, thiophene, fluorene, typically 9,9-dialkyl substituted fluorene eg. 9,9-dihexylfluorene, divinylbenzene, distyrylethylene, divinylpyridine, pyrimidine, triazine, divinylthiophene, oxadiazole, coronene, or a fluorescent dye or marker compound or a metallic chromophore such as a lanthanide, or iridium complex, or a metalloporphyrin. These various rings may be substituted,

10   for example by C_1 to C_{15} alkyl or alkoxy groups.

It is possible to control the electron affinity of the dendrimers by the addition to the chromophores of electron-withdrawing groups, for example cyano and sulfone which are strongly electron-withdrawing and optically transparent in the spectral region we are interested in. Further details of this and other modifications of the

15   dendrimers can be found in WO99/21935 to which reference should be made.

The dendrimers for the present invention can be prepared in a similar manner to those described in WO99/21935. In a preferred embodiment, the dendrons are first prepared. The dendrons are then reacted with a functionality to form the core. For example a dendron is prepared with an aldehyde at the foci which can then be

20   condensed with pyrrole to form a porphyrin cored dendrimer.

The dendrimer can be incorporated into a light emitting diode (LED), also known as an electroluminescent (EL) device, in a conventional manner. In a preferred embodiment the dendrimer acts as the light emitting element. By suitable selection of dendrons and surface groups the dendrimers can be made soluble in

25   conventional solvents such as toluene, THF, water and alcoholic solvents such as methanol. In its simplest form, an organic light emitting or electroluminescent device can be formed from a light emitting layer sandwiched between two electrodes, at least one of which must be transparent to the emitted light. Such a device can have a conventional arrangement comprising a transparent substrate layer, a transparent

30   electrode layer, a light emitting layer and a back electrode. For this purpose the

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standard materials can be used. Thus, typically, the transparent substrate layer is typically made of glass although other transparent materials such as PET can also be used.

The anode which is generally transparent is preferably made from indium tin

5   oxide (ITO) although other similar materials including indium oxide/tin oxide, tin oxide/antimony, zinc oxide/aluminum, gold and platinum can also be used. Conducting polymers such as PANI (polyaniline) or PEDOT can also be used.

The cathode is normally made of a low work function metal or alloy such as Al, Ca, Mg, Li, or MgAl or optionally with an additional layer of LiF. As is well

10   known, other layers may also be present, including a hole transporting material and/or an electron transporting material. In an alternative configuration, the substrate may be an opaque material such as silicon and the light is emitted through the opposing electrode.

The dendrimers of the present invention can be deposited by known solution

15   processing methods, such as spin-coating, printing, dip-coating. The dendrimer can be deposited as a neat film or as a blend with other organic materials (dendrimers, polymers and/or molecular compounds). Other organic layers, for example charge transporting materials, can be deposited on top of the dendrimer film by evaporation, or by solution processing from a solvent in which the first layer is not soluble. The

20   film thickness is typically 10 nm to 1000 nm, preferably less than 200 nm, more preferably less than 120 nm.

The dendrimers can also be used in other semiconducting devices which including photodiodes, solar cells, FET or a solid state triode.

The present invention will be further illustrated in the following Examples

25   with reference to the accompanying Figures, in which:

Figure 1 shows a schematic diagram of a dendrimer;
Figure 2 shows the reaction scheme for the preparation of higher generation dendritic intermediates;
30   Figure 3 shows two first generation dendrimers;

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Figure 4 shows a second generation Zn-porphyrin cored dendrimer;

Figures 5 - 8 show different fluorene-based core dendrimers and the preparation steps.

5

Example 1

G0-Br (1)

4-(2'-Ethylhexyloxy)phenylbromide

Sodium hydride (60% dispersion in oil, 17.4 g, 435 mmol) was added in portions to a

10   cold (ice-bath) solution of 4-bromophenol (49.0 g, 283 mmol) in dry DMF (780 cm^3). The mixture was stirred at that temperature for 2 h and the ice bath was removed. A solution of 2-ethylhexylbromide (54.4 cm^3, 306 mmol) in 150 cm^3 of dry DMF was added dropwise through an addition funnel to the reaction mixture and the reaction was stirred at room temperature overnight (21 h). The resultant mixture was

15   diluted with water (400 cm^3) and ether (500 cm^3). The two phases were separated. The aqueous layer was extracted with ether (3 x 300 cm^3) and the organic portion and the ether extracts were dried over anhydrous MgSO$_4$, filtered and the filtrate was collected and evaporated under reduced pressure to leave yellow oil. Column chromatography over silica gel (half amount each time) with light petroleum as

20   eluent afforded $\underline{1}$ (54.1 g, 67%) as colourless oil; λ_{max}(CH$_2$Cl$_2$)/nm 284 (ε/dm^{3}mol^{-1}cm^{-1} 1251), and 291sh (1001); δ_H(400 MHz; CDCl$_3$) 0.83-0.97 (6 H, m, Me), 1.30-1.57 (8 H, m, CH$_2$), 1.68-1.79 (1 H, m, CH), 3.78-3.84 (2 H, m, ArOCH$_2$), 6.74-6.80 (2 H, m, ArH), and 7.33-7.40 (2 H, m, ArH); δ_C(100 MHz; CDCl$_3$) 11.1, 14.1, 23.0, 23.8, 29.1, 30.4, 39.3, 70.7, 112.4, 116.3, 132.1, and 158.5.

25

Example 2

G0-SnBu$_3$ (2)

1-(2'-Ethylhexyloxy)-4-(tri-n-butyl)stannylbenzene

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Tert-butyl lithium (1.7 M, 21.7 cm^3, 36.8 mmol) was added slowly over 10 min to a cold (dry-ice/acetone bath) solution of **G0-Br 1** (7.00 g, 24.5 mmol) in 54 cm^3 of ether under argon atmosphere. The mixture was stirred at -78 °C for 2 h and tri-*n*-butyl tin chloride (10 cm^3, 36.8 mmol) was added dropwise over 5 min to the

5   mixture, which was stirred at -78 °C for 1 h before being removed from the dry-ice/acetone bath. The mixture was stirred at room temperature for a further 3 h before being quenched with 10% of $NH_4Cl_{(aq)}$ (20 cm^3). The aqueous layer was separated and extracted with dichloromethane (DCM) (2 x 10 cm^3). The DCM extracts and the ether portion were then dried (MgSO$_4$) and filtered. The solvents were removed

10   completely. Kugolrohr distillation removed the excess tri-*n*-butyl tin chloride to leave 12.0 g (99%) of **2** as a light yellow oil; λ_{max}(CH$_2$Cl$_2$)/nm 277 (ε/dm^{3}mol^{-1}cm^{-1} 826), and 284sh (660); δ_H(200 MHz; CDCl$_3$) 0.81-1.09 (15 H, m, Me), 1.21-1.81 (27 H, m, CH$_2$ & CH), 3.84 (2 H, m, ArOCH$_2$), 6.91 (2 H, m, ArH), and 7.36 (2 H, m, ArH).

15

Example 3

G1-CHO (3)

<u>3,5-Di[4'-(2"-ethylhexyloxy)phenyl]benzaldehyde</u>

Method 1:

20   A mixture of **2** (8.50 g, 17.2 mmol), 3,5-di-bromobenzaldehyde (1.18 g, 4.47 mmol), CuI (790 mg, 4.15 mmol), tetrakis(triphenylphosphine) palladium (0) (790 mg, 0.684 mmol) and 20 cm^3 of distilled triethylamine was heated at reflux for 14 h under argon. The reaction mixture was allowed to cool and then filtered through a plug of silica gel using DCM as eluent. The filtrate was collected and the solvent was

25   completely removed to yield a brown yellow oil. The residue was purified by column chromatography over silica using ethyl acetate-light petroleum (0:1 to 1:10) as eluent to give **3** as a colourless oil (1.91 g, 83%); ν_{max}/cm^{-1} (neat) 1700 (C=O); λ_{max}(CH$_2$Cl$_2$)/nm 247 (ε/dm^{3}mol^{-1}cm^{-1} 22406), 274 (27554), and 339sh (1817); δ_H(400 MHz; CDCl$_3$) 0.88-1.01 (12 H, m, Me), 1.30-1.61 (16 H, m, CH$_2$), 1.73-1.84

(2 H, m, CH), 3.94 (4 H, m, ArOCH$_2$), 7.04 (4 H, m, ArH), 7.62 (4 H, m, ArH), 7.99

(3 H, s, ArH), and 10.13 (1 H, s, CHO); δ_C(100 MHz; CDCl$_3$) 11.1, 14.1, 23.1, 23.9,

29.1, 30.5, 39.4, 70.6, 115.0, 126.0, 128.2, 130.8, 131.9, 137.4, 142.3, 159.6, and

192.5; m/z [CI(NH$_3$)] 533 (MNH$_4^+$), and 515 (M$^+$).

Method 2:

A mixture of **4B** (213 mg, 0.851 mmol), 3,5-di-bromobenzaldehyde (98 mg, 0.370

mmol), tetrakis(triphenylphosphine) palladium (0) (30 mg, 0.026 mmol), 2 M

Na$_2$CO$_{3(aq)}$ (0.5 cm^3), EtOH (0.5 cm^3) and toluene (1.1 cm^3) was degassed and heated

at reflux (with bath temperature of 96 °C) under argon for 18 h. The mixture was

allowed to cool. Water (4 cm^3) and ether (5 cm^3) were added to the mixture. The two

phases were separated. The aqueous layer was extracted with ether (3 x 5 cm^3). The

organic layer and the ether extracts were combined and dried over anhydrous

magnesium sulfate and filtered. The solvents were completely removed. The residue

was purified by column chromatography over silica gel using light petroleum (60-80

°C) as eluent to give 172 mg (90%) of **3** as a colourless oil.

Example 4

G0-B(X)$_2$ (4)

4-(2'-Ethylhexyloxy)phenylboronic acid

Tert-butyl lithium (1.7 M, 66.0 cm^3, 112 mmol) was added carefully to a cold (dry-

ice/acetone bath) solution of **G0-Br 1** (20.0 g, 70.1 mmol) in 300 cm^3 of anhydrous

THF under an argon atmosphere. The mixture was stirred at -78 °C for 1 h and then

tri-methyl borate (57.2 cm^3, 421 mmol) was added slowly to the cold mixture. The

reaction was stirred at -78 °C for 2 h before being removed from the dry-ice/acetone

bath. The mixture was then stirred at room temperature for further 2.5 h before being

quenched with 3 M HCl$_{(aq)}$ (30 cm^3). The two layers were separated. The aqueous

layer was extracted with DCM (3 x 30 cm^3). The organic layer and the DCM extracts

were combined and dried over anhydrous magnesium sulfate, filtered and the

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solvents were completely removed. Purification by column chromatography over

silica gel using ethyl acetate-light petroleum (1:10), and then ethyl acetate-DCM (0:1

to 1:3) as eluent gave two major bands; less polar compound **4A**, 6.44 g as a

colourless oil; δ_H(200 MHz; CDCl$_3$) 0.81-1.05 (6 H, m, Me), 1.22-1.62 (8 H, m,

5   CH$_2$), 1.68-1.88 (1 H, m, CH), 3.91 (2 H, m, ArOCH$_2$), 6.98 (2 H, m, ArH), and 7.77

(2 H, m, ArH); and more polar compound, a trimer, **4B**, 8.40 g as a colourless oil;

δ_H(200 MHz; CDCl$_3$) 0.85-1.07 (6 H, m, Me), 1.30-1.64 (8 H, m, CH$_2$), 1.70-1.90 (1

H, m, CH), 3.95 (2 H, m, ArOCH$_2$), 7.03 (2 H, m, ArH), and 8.18 (2 H, m, ArH).

*Note: either compound **4A** or **4B** can be used in the reaction to form the next*

10   *generation dendrons. In either case of **4A** or **4B** being a dimer the number of protons*

in the ^{1}H NMR should be considered as a ratio.

Example 5
G1-Br (5)

15   3,5-Di[4'-(2"-ethylhexyloxy)phenyl]phenyl bromide

A mixture of the boronic acid **4B** (7.9 0g, 31.6 mmol), 1,3,5-tribromobenzene (4.53

g, 14.4 mmol), tetrakis(triphenylphosphine) palladium (0) (1.16 g, 1.00 mmol), 2 M

Na$_2$CO$_3$(aq) (15 cm^3), EtOH (15 cm^3) and toluene (43 cm^3) was degassed and heated at

reflux (with bath temperature of 101 °C) under argon for 22 h. The mixture was

20   allowed to cool. Water (20 cm^3) and ether (30 cm^3) were added to the mixture. The

two phases were separated. The aqueous layer was extracted with ether (3 x 20 cm^3).

The organic layer and the ether extracts were combined and dried over anhydrous

magnesium sulfate and filtered. The solvents were completely removed. The residue

was purified by column chromatography over silica gel using light petroleum (60-80

25   °C) as eluent to give 6.04 g (74%) of **5** as a colourless oil; δ_H(200 MHz; CDCl$_3$) 0.82-

1.02 (12 H, m, Me), 1.26-1.60 (16 H, m, CH$_2$), 1.70-1.83 (2 H, m, 2 x CH), 3.90 (4

H, m, ArOCH$_2$), 6.99 (4 H, m, ArH), 7.54 (4 H, m, ArH), and 7.62 (3 H, s, ArH); *m/z*

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[MALDI] 566 (M⁺). In addition, 910 mg (9%) of the tris-substituted compound as a colourless oil was isolated; δ_H(200 MHz; CDCl₃) 0.82-1.02 (18 H, m, Me), 1.25-1.63 (24 H, m, CH₂), 1.70-1.83 (3 H, m, CH), 3.90 (6 H, m, ArOCH₂), 7.01 (6 H, m, ArH), 7.62 (6 H, m, ArH), and 7.65 (3 H, s, ArH); m/z [APCI⁺] 692 (MH⁺).

5

Example 6

G1-BX₂ (6)

Tert-butyl lithium (1.7 M, 3.0 cm³, 5.15 mmol) was added to a cold (dry-ice/acetone bath) solution of aryl bromide **5** (1.82 g, 3.22 mmol) in 18 cm³ of anhydrous THF under argon atmosphere. The reaction mixture, changing to a deep reddish brown

10   was stirred at -78 °C for 1 h. Tri-*n*-butyl borate (5.2 cm³, 19.3 mmol) was added slowly to the mixture and the reaction was stirred at -78 °C for 1 h before being removed from the dry-ice/acetone bath. The mixture was then stirred at room temperature for further 3.5 h before being quenched with 3 M HCl₍aq₎ (7 cm³). The

15   two layers were separated. The aqueous layer was extracted with DCM (3 x 5 cm³). The organic layer and the DCM extracts were dried over anhydrous magnesium sulfate and filtered. The solvents were completely removed. Purification on silica gel column using ethyl acetate-light petroleum (1:10), and then ethyl acetate-DCM (1:4) as eluent gave 1.63 g (96%) of **6** as a colourless oil. The structure of **6** has not been

20   fully determined however can be used to form higher generation dendrons in excellent yield.

Example 7

G2-CHO (7)

25   3,5-Di{3',5'-di[4"-(2'''-ethylhexyloxy)phenyl]phenyl}benzaldehyde

A mixture of the **G1-BX₂ 6** (6.30 g, 11.9 mmol), 3,5-dibromobenzaldehyde (1.04 g, 3.96 mmol), tetrakis(triphenylphosphine) palladium (0) (320 mg, 0.277 mmol), 2 M Na₂CO₃₍aq₎ (11 cm³), EtOH (11 cm³) and toluene (26 cm³) was degassed and heated at

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reflux (with bath temperature of 95 °C) under argon for 17 h. The resultant orange

mixture was allowed to cool. Water (20 cm³) and ether (20 cm³) were added to the

mixture. The two phases were separated. The aqueous layer was extracted with ether

(3 x 30 cm³). The organic layer and the ether extracts were dried over anhydrous

5   magnesium sulfate and filtered. The solvents were completely removed. The residue

was purified by column chromatography over silica gel using ethyl acetate-light

petroleum (0:1 to 1:40) as eluent to afford 4.00 g (94%) of $\underline{7}$ as a colourless oil;

δ_H(200 MHz; CDCl₃) 0.83-1.05 (24 H, m, Me), 1.25-1.60 (32 H, m, CH₂), 1.65-1.89

(4 H, m, CH), 3.91 (8 H, m, ArOCH₂), 7.03 (8 H, m, ArH), 7.65 (8 H, m, ArH), 7.79

10   (6 H, s, ArH), 8.22 (2 H, s, ArH), 8.25 (1 H, s, ArH), and 10.22 (1 H, s, CHO).

Example 8

G2-Br (8)

3,5-Di{3',5'-di[4"-(2"'-ethylhexyloxy)phenyl]phenyl}phenyl bromide

15   A mixture of the $\underline{6}$ (313 mg, 0.591 mmol), 1,3,5-tribromobenze (71.5 mg, 0.227

mmol), tetrakis(triphenylphosphine) palladium (0) (18.3 mg, 0.016 mmol), 2 M

Na₂CO₃(aq) (0.3 cm³), EtOH (0.3 cm³) and toluene (0.7 cm³) was degassed and heated

at reflux under argon for 24 h. The resultant orange mixture was allowed to cool and

passed through a plug of silica gel using ether as eluent. The filtrate was collected

20   and the solvents were completely removed. The residue was purified by column

chromatography over silica gel using light petroleum as eluent to afford 213 mg

(83%) of $\underline{8}$ as a colourless oil; δ_H(200 MHz; CDCl₃) 0.83-1.05 (24 H, m, Me), 1.26-

1.64 (32 H, m, CH₂), 1.68-1.89 (4 H, m, CH), 3.94 (8 H, m, ArOCH₂), 7.05 (8 H, m,

ArH), 7.61-7.94 (16 H, m, ArH), and 8.04 (1 H, s, ArH).

25

Example 9

G1-DSB (9)

1,4-Bis{3',5'-di[4"-(2"'-ethylhexyloxy)phenyl]styryl}benzene

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Anhydrous THF was added to a mixture of **G1-CHO 3** (302 mg, 0.587 mmol), 1,4-bis(methylenedimethylphosphonate)benzene (91 mg, 0.281 mmol) and potassium *tert*-butoxide (79 mg, 0.704 mmol) at room temperature under argon. After stirring for 19 h, the mixture was quenched with 0.5 cm^3 of water. The mixture was dried

5   over anhydrous magnesium sulfate and passed through a plug of silica gel using DCM as eluent. The filtrate was collected and the solvent was removed. The mixture was purified by column chromatography over silica gel with ethyl acetate-light petroleum (1:10) as eluent to give the **G1-DSB** as a mixture of isomers.

10   Isomerisation was carried out by heating the mixture of the **G1-DSB**, catalytic amount of I$_2$ and toluene (3 cm^3) at reflux for 4 h. The mixture was allowed to cool, washed with aqueous sodium metabisulfite solution (10%, 1 x 5 cm^3), dried (MgSO$_4$) and filtered and the solvent was completely removed. The mixture was purified by column chromatography over silica gel using DCM-petroleum (1:4) as eluent to give

15   179 g (58%) of **9**; δ_H(200 MHz; CDCl$_3$) 0.85-1.05 (24 H, m, Me), 1.26-1.67 (32 H, m, CH$_2$), 1.69-1.90 (4 H, m, CH), 3.94 (8 H, m, ArOCH$_2$), 7.05 (8 H, m, ArH), 7.28 (4 H, m, ArH), 7.55-7.72 (18 H, ArH & vinyl H); *m/z* [MALDI] 1099 (M$^+$).

Example 10

20   **G1-Zn-Porphyrin (10)**
5,10,15,20-Tetra{3',5'-di[4''-(2'''-ethylhexyloxy)phenyl]phenyl}porphinatozinc (II)
A mixture of the **G1-CHO 3** (420 mg, 0.816 mmol), distilled pyrrole (0.12 cm^3, 1.73 mmol), zinc acetate dihydrate (730 mg, 3.33 mmol) and 7 cm^3 of propionic acid was heated at reflux for 5 h. The mixture was allowed to cool and passed through a

25   column of silica gel using DCM-petroleum (1:4) as eluent. The main band was collected and the solvents were removed. The residue was purified by column chromatography using silica gel with DCM-light petroleum (1:4) as eluent to give 120 mg (6%) of **10** as a blue purple solid; λ_{max}/nm (thin film) 270, 435, 556, and 595; δ_H(200 MHz; CDCl$_3$) 0.81-1.01 (48 H, m, Me), 1.20-1.62 (64 H, m, CH$_2$), 1.63-1.86

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(8 H, m, CH), 3.90 (16 H, m, ArOCH$_2$), 7.05 (16 H, m, ArH), 7.85 (16 H, m, ArH), 8.18 (4 H, s, ArH), 8.43 (8 H, m, ArH), and 9.20 (8 H, s, β-pyrrolic H); *m/z* [MALDI] 2311 (M$^+$).

5 **Example 11**

G2-Zn-Porphyrin (11)

5,10,15,20-Tetra(3',5'-di{3",5"-di[4'''-(2''''-ethylhexyloxy)phenyl]phenyl}phenyl)porphinato zinc (II)

A mixture of the **G2-CHO** 7 (583 mg, 0.542 mmol), distilled pyrrole (0.09 cm^3, 1.30

10 mmol), zinc acetate dihydrate (500 mg, 2.28 mmol) and 4.6 cm^3 of propionic acid was heated at reflux for 18 h and then allowed to cool to room temperature. The mixture was passed through a column of silica gel using DCM-light-petroleum (1:4) as eluent. The main band was collected and the solvents were removed. The residue was purified by column chromatography using silica gel with DCM-light petroleum

15 (1:4) as eluent to give ≅130 mg (≅5%) of **11** as a blue purple solid; λ$_{max}$/nm (thin film) 270, 433, 554, and 592; δ$_H$(200 MHz; CDCl$_3$) 0.75-1.01 (96 H, m, Me), 1.18-1.59 (128 H, m, CH$_2$), 1.60-1.81 (16 H, m, CH), 3.83 (32 H, m, ArOCH$_2$), 6.94 (32 H, m, ArH), 7.62 (32 H, m, ArH), 7.52 (8 H, s, ArH), 8.00 (16 H, m, ArH), 8.43 (4 H, s, ArH), 8.65 (8 H, m, ArH), and 9.26 (8 H, s, β-pyrrolic H).

20

Example 12

25 This Example of the synthesis of first generation dendrimers follows Figure 5, the compound numbering being as given.

9-Propylfluorene (2) 9,9-Dipropylfluorene (3) and 2,7-Dibromo-9,9-dipropylfluorene (4) can be obtained following Kelley et al, J. Chem. Research (M) 1997, 2701.

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Compound (5)

tert-Butyllithium (1.7 M in pentane, 8.5 cm³, 0.015 mol) was added dropwise to a
solution of 2,7-dibromo-9,9-dipropylfluorene (4) (2.50 g, 6.00 mmol) in dry THF

5   (100 cm³) at –78 °C under argon. The solution was stirred for 1 h and 2-isopropoxy-
4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.0 g, 0.022 mol) was added. The solution
was allowed to warm to RT and stirred for 3 d then water (100 cm³) and diethyl ether
(100 cm³) added. The aqueous layer was separated, washed with diethyl ether (100
cm³) and the organic layers combined, dried over anhydrous magnesium sulphate,

10 filtered and concentrated to a pale yellow powder which was purified by column
chromatography [silica gel, DCM : petroleum ether 40-60 °C 1 : 4 eluting to 1 : 2]
and recrystallisation from DCM : methanol to yield a white crystalline solid.

Yield 1.7 g (56 %); δ_H(200 MHz; CDCl₃) 7.75 (m, 6 H), 2.0 (t, 4 H) , 1.39 (s, 24 H),
0.62 (m, 10 H); *m/z* [APCI⁺] 503 (M⁺), 125, 124, 123, 122; v_{max}(KBr)/cm⁻¹ 3436, 2959,

15 1608, 1573, 1475, 1424, 1348, 1239, 1147, 1112, 964, 846, 701

Compound (8) can be obtained according to Beaupré et al, Macromol. Rapid Commum.,
2000, 21, 1013.

20 **2,7-Bis{3,5-di[4-(2-ethylhexyloxy)phenyl]phen-1-yl}-9,9-dihexylfluorene (10)**
A mixture of the G1-boronic acid (9) [G1-BX₂ of Example 6] (190 mg 3.58 × 10⁻⁴
mol), 2,7-dibromo-9,9-dihexylfluorene (7) (71 mg, 1.4 × 10⁻⁴ mol),
tetrakis(triphenylphosphine) palladium (0) (13 mg, 1.1 × 10⁻⁵ mol), aqueous sodium
carbonate (2 M, 0.2 cm³) in toluene (0.5 cm³) and ethanol (0.8 cm³) was heated under

25 reflux for 18 h under argon. Water (5 cm³) and DCM (15 cm³) were added and the
organic layer separated, dried over anhydrous magnesium sulphate, filtered and
concentrated onto silica gel for purification by column chromatography [silica gel,
petroleum ether 40-60 °C : DCM 2 : 1] to yield a white glassy solid.

Yield 105 mg (58%); (Found: C, 85.77; H, 9.39. requires C, 85.66; H, 9.43); δ_H(200

30 MHz; CDCl₃) 7.62-7.90 (m, 20 H), 7.08 (d, 8 H), 3.80 (d, 8 H), 2.12 (t, 4 H), 1.80 (t, 4

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H), 1.80 (quint, 4 H), 0.72-1.65 (m, 78 H); v_{max}(KBr)/cm^{-1} 3436, 2926, 1609, 1512. 1439, 1285, 1250, 1176, 1033, 822; m/z [MALDI] 1304 (M$^+$)

Example 13

5

2-[4,4''-Bis-(2-ethyl-hexyloxy)-1,1',3',1''-terphenyl-5'-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12)

tert-Butyllithium (1.7M solution in pentane, 5.35 cm^3, 9.11 x 10^{-3} mol) was added slowly to a solution of the G1-bromide.(11, which is the same as 5 prepared in

10 Example 5) (3.43 g, 6.07 x 10^{-3} mol) in dry THF (50 cm^3) at –78 °C under argon. The solution was stirred at –78 °C for 1 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.0 cm^3, 22 mmol) was added and the solution allowed to warm to RT and stirred for 3 d. Diethyl ether (75 cm^3) was added and the solution washed with water (2 x 30 cm^3). The aqueous layers were combined and washed with diethyl

15 ether (2 x 50 cm^3), the organic layers combined, dried over anhydrous magnesium sulphate, filtered and concentrated to a pale yellow oil which was purified by column chromatography [silica gel, petroleum ether 60-80 °C : DCM 1 : 1 eluting to DCM] to give a white crystalline solid.

Yield 2.4 g (64 %); δ_H(200 MHz; CDCl$_3$) 7.98 (d, 2 H), 7.84 (m, 1 H), 7.63 (d, 4 H),

20 7.00 (d, 4 H), 3.91 (d, 4 H), 1.78 (m, 2 H), 1.30-1.60 (m, 28 H), 0.98 (t, 12 H)

2,7-Bis{3,5-di[4-(2-ethylhexyloxy)phenyl]phen-1-yl}-fluorene (14)

A mixture of 2,7-dibromofluorene (13) (Kelley et al loc. cit) (100 mg, 3.10 × 10^{-4} mol), G1-borolane (12) (0.47 g, 7.7 × 10^{-4} mol),

25 tetrakis(triphenylphosphine)palladium (0) (15 mg, 1.3 × 10^{-5} mol), aqueous sodium carbonate (2M, 0.5 cm^3) and ethanol (0.3 cm^3) was heated under reflux for 24 h under argon. DCM (20 cm^3) and dilute HCl$_{(aq)}$ (3M, 15 cm^3) were added and the organic layer separated, washed with water (2 × 10 cm^3), dried over anhydrous magnesium sulphate, filtered and concentrated to a brown oil which was purified by column

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chromatography [silica gel, petroleum ether 40-60 °C eluting to 4 : 1 petroeum ether 40-60 °C : DCM] to yield a white, glassy solid.

Yield 210 mg (60 %)

5   *2,7-Bis{3,5-di[4-(2-ethylhexyloxy)phenyl]phen-1-yl}-9,9-dipropylfluorene (16)*

A mixture of the G1-Br (11) (Example 5) (500 mg, 8.85 x 10^{-4} mol), compound 5 (150 mg, 2.98 x 10^{-4} mol), tetrakis(triphenylphosphine)palladium (0) (70 mg, 8.1 x 10^{-5} mol) in toluene (2.5 cm^3), methanol (0.8 cm^3) and aqueous sodium carbonate (2M, 2.5 cm^3) was heated under reflux for 20 h under argon. DCM (20 cm^3) and

10 dilute HCl$_{(aq)}$ (3M, 20 cm^3) were added, the aqueous layer separated, washed with DCM (10 cm^3), the organic layers combined, dried over anhydrous magnesium sulphate, filtered and concentrated to a yellow oil which was purified by column chromatography [petroleum ether 60-80 °C : DCM 4 : 1 eluting to 2 : 1] to yield a glassy white solid.

15 Yield 0.27 g (74 %); (Found: C, 85.09; H, 9.46. requires C, 85.66; H, 9.09); δ_H(200 MHz; CDCl$_3$) 7.62-7.90 (m, 20 H), 7.04 (d, 8 H), 3.92 (d, 8 H), 2.12 (t, 4 H), 1.80 (t, 4 H), 1.25-1.65 (m, 32 H), 0.95 (m, 24 H), 0.72 (m, 10 H); v_{max}(KBr)/cm^{-1} 2926, 1608, 1512, 1465, 1439, 1250, 1176, 1035, 822

20 *2,7-Bis{3,5-di[4-(butyloxy)phenyl]phen-1-yl}-9,9-dihexylfluorene (17)*

A mixture of the G1-bromide (15) (350 g, 7.68 x 10^{-4} mol), compound 8 (150 mg, 2.56 x 10^{-4} mol), tetrakis(triphenylphosphine)palladium (0) (50 mg, 5.3 x 10^{-5} mol) in toluene (2.5 cm^3), methanol (0.8 cm^3) and aqueous sodium carbonate (2M, 0.8 cm^3) was heated under reflux for 20 h under argon. DCM (20 cm^3) and dilute HCl$_{(aq)}$ (3M,

25 20 cm^3) were added, the aqueous layer separated, washed with DCM (10 cm^3), the organic layers combined, dried over anhydrous magnesium sulphate, filtered and concentrated to a yellow oil which was purified by column chromatography [petroleum ether 60-80 °C : DCM 6 : 1 eluting to 4 : 1] to yield a glassy white solid.

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Yield 149 mg (54 %); δ_H(200 MHz; CDCl$_3$) 7.62-7.90 (m, 20 H), 7.04 (d, 8 H), 4.05 (t, 8 H), 2.05 (t, 4 H), 1.81 (quint, 8 H), 1.51 (quint, 8 H), 1.05 (m, 10 H), 0.72 (m, 10 H); v_{max}(KBr)/cm^{-1} 2928, 1609, 1512, 1473, 1440, 1284, 1250, 1177, 823.

5   Figure 5:

2,7-Bis{3,5-di[4-(butoxy)phenyl]phen-1-yl}-9,9-dipropylfluorene (18)

A mixture of compound 5 (150 mg, 2.98 × 10^{-4} mol, compound 15 (400 mg, 8.80 × 10^{-4} mol), tetrakis(triphenylphosphine)palladium (0) (70 mg, 8.1 × 10^{-5} mol) in toluene (2.5 cm^3), aqueous sodium carbonate (2 M, 0.8 cm^3) and ethanol (4 cm^3) was

10 heated under reflux for 3 d under argon. DCM (10 cm^3) and dilute HCl$_{(aq)}$ (3 M, 5 cm^3) were added, the aqueous layer separated, washed with DCM (2 × 5 cm^3), the organic layers combined, dried over anhydrous magnesium sulphate, filtered, concentrated to a pale yellow oil and purified by column chromatography [petroleum ether 40-60 °C : DCM 2 : 1] to yield a white powder.

15 Yield 158 mg (53 %); (Found: C, 85.45; H, 7.95. requires C, 85.67; H, 7.90); δ_H(200 MHz; CDCl$_3$) 7.72 (m, 20 H), 7.05 (m, 7 H), 4.08 (t, 8 H), 2.50 (t, 4 H), 1.82 (quint, 8 H), 1.54 (quint, 8 H), 1.02 (t, 12 H), 0.72 (m, 10 H); v_{max}(KBr)/cm^{-1} 3436, 2955, 1609, 1512, 1473, 1439, 1283, 1249, 1176, 822; *m/z* [MALDI] 994 (M$^+$)

20 The G1-bromide (15) used in preparation of both (17) and (18)was prepared as follows and as shown in Figure 8.:

Figure 8:

G0-Br 4-Butoxyphenylbromide, 32

25 A suspension of powered KOH (48 g, 856 mmol) in anhydrous DMSO (dried over molecular sieve) (250 cm^3) was completely degassed. *p*-Bromophenol (34.6 g, 200 mmol) and 1-bromobutane (142 cm^3, 800 mmol) were added to the mixture. The reaction was stirred at room temperature for 21 h under Ar$_{(g)}$ before being cooled in a ice-bath. Ice/water (~ 200 cm^3) was added to the mixture. The two layers were

30 separated. The aqueous layer was extracted with petroleum (40-60 °C) (3 x 100 cm^3).

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The organic layer and the petroleum extracts were combined, washed with brine (1 x 150 cm^3) and dried (MgSO$_4$). The solvent was removed to leave a pale yellow oil. Purification by column chromatography over silica gel using light petroleum gave a mixture of the 4-butoxyphenylbromide and small amount of 1-bromobutane which

5   was removed by high vacuum to leave 44.1 g (96%) of $\underline{32}$ as a pale yellow oil; (Found: C, 52.3; H, 5.8. C$_{10}$H$_{13}$BrO requires C, 52.4; H, 5.7%); δ_H(400 MHz; CDCl$_3$) 0.99 (3 H, t, J 7.4 Hz, Me), 1.46-1.58 (2 H, m, CH$_2$), 1.72-1.83 (2 H, m, CH$_2$), 3.93 (2 H, t, J 6.5 Hz, ArOCH$_2$), 6.79 (2 H, m, ArH), and 7.37 (2 H, m, ArH); δ_C(101 MHz; CDCl$_3$) 13.8, 19.2, 31.2, 67.9, 112.5, 116.3, 132.1, and 158.2; m/z [EI] 228,

10   230 (M$^+$).

G0-BOR$_2$

1-Butoxy-4-(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)benzene, 33

Tert-butyl lithium (1.5 M, 23.4 cm^3, 35.1 mmol) was added to a cold (dry-ice/acetone

15   bath) solution of $\underline{32}$ (5.00 g, 21.9 mmol) in 90 cm^3 of anhydrous THF under an argon atmosphere. The mixture was stirred at -78 °C for 1 h and then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5.4 cm^3, 26.3 mmol) was added rapidly to the cold mixture. The reaction was stirred at -78 °C for 2 h and the dry-ice/acetone bath was removed. The mixture was then stirred at room temperature for further 22 h before

20   being quenched with H$_2$O (40 cm^3). The two layers were separated. The aqueous layer was extracted with ether (3 x 30 cm^3). The organic layer and the ether extracts were combined and dried over anhydrous magnesium sulfate and the solvents were completely removed. Purification of these crude mixture by column chromatography over silica gel using ethyl acetate-light petroleum (0:1 to 1:10) as eluent gave 4.09 g

25   (68%) of $\underline{33}$ as a light yellow oil; (Found: C, 69.5; H, 9.1. C$_{16}$H$_{25}$BO$_3$ requires C, 69.6; H, 9.1; N, 5.0%); δ_H(400 MHz; CDCl$_3$) 0.99 (3 H, t, J 7.4 Hz, Me), 1.35 (12 H, s, Me), 1.46-1.59 (2 H, m, CH$_2$), 1.73-1.84 (2 H, m, CH$_2$), 4.00 (2 H, t, J 6.5 Hz, ArOCH$_2$), 6.90 (2 H, m, ArH), and 7.76 (2 H, m, ArH); δ_C(101 MHz; CDCl$_3$) 13.8, 19.2, 24.8, 31.2, 67.4, 83.5, 113.8, 136.5, and 161.7; m/z [EI] 276 (M$^+$).

G1-Br

3,5-Di(4'-butoxyphenyl)phenyl bromide, 15 (also in Figure 5)

A mixture of the boronic compound **33** (3.80 g, 13.8 mmol), 1,3,5-tribromobenzene

5   (1.97 g, 6.25 mmol), tetrakis(triphenylphosphine) palladium (0) (400 mg, 0.346

mmol), 2 M $Na_2CO_{3(aq)}$ (6 cm³), EtOH (6 cm³) and toluene (18 cm³) was degassed

and then heated at reflux under argon for 69 h. The mixture was allowed to cool.

Water (5 cm³) and ether (5 cm³) were added to the mixture. The two phases were

separated. The aqueous layer was extracted with ether (3 x 20 cm³). The organic layer

10   and the ether extracts were combined and dried over anhydrous magnesium sulfate.

The solvents were completely removed. The residue was purified by column

chromatography over silica gel using light DCM-light petroleum (60-80 °C) (0:1 to

1:20) as eluent to give 1.71 g (60%) of **15** as a white solid; (Found: C, 68.7; H, 6.5.

$C_{26}H_{29}BrO_2$ requires C, 68.9; H, 6.5%); δ_H(400 MHz; CDCl₃) 0.99-1.09 (6 H, m,

15   Me), 1.50-1.63 (4 H, m, CH₂), 1.79-1.90 (4 H, m, CH₂), 4.03 (4 H, t, J 6.5 Hz,

ArOCH₂), 7.00 (4 H, m, ArH), 7.54 (4 H, m, ArH), and 7.63 (3 H, m, ArH); δ_C(101

MHz; CDCl₃) 13.9, 19.3, 31.3, 67.8, 114.8, 123.2, 123.8, 127.8, 128.2, 132.0, 143.2,

and 159.2; m/z [EI] 452, 454 (M⁺).

Besides, 717 mg (22%) of tri-substituted product was isolated as a white solid;

20   (Found: C, 82.3; H, 8.1. $C_{36}H_{42}O_3$ requires C, 82.7; H, 8.1%); δ_H(500 MHz; CDCl₃)

1.02 (9 H, t, J 7.4 Hz, Me), 1.50-1.60 (6 H, m, CH₂), 1.78-1.89 (6 H, m, CH₂), 4.04 (6

H, t, J 6.5 Hz, ArOCH₂), 7.02 (6 H, m, ArH), 7.63 (6 H, m, ArH), and 7.67 (3 H, m,

ArH); δ_C(126 MHz; CDCl₃) 13.8, 19.2, 31.2, 67.7, 114.7, 123.6, 128.2, 133.5, 141.7,

and 159.8; m/z [MALDI] 522, 523, 524 (M⁺).

25

Example 14

This follows Figure 6.

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2,7-Bis(3,5-di{3,5-di[4-(2-ethylhexyloxy)phenyl]phen-1-yl}phen-1-yl)-9,9-
dihexylfluorene (20)

A mixture of the G2-bromide (**19** [which is the same as **8** prepared in Example 8]

5   (1.00 g, 8.89 x 10^{-4} mol), compound **8** (173 mg, 2.96 x 10^{-4} mol),

tetrakis(triphenylphosphine)palladium (0) (70 mg, 8.1 x 10^{-5} mol) in toluene (3 cm^3),

methanol (2 cm^3) and aqueous sodium carbonate (2M, 2 cm^3) was heated under

reflux for 20 h under argon. DCM (20 cm^3) and dilute $HCl_{(aq)}$ (3M, 20 cm^3) were

added, the aqueous layer separated, washed with DCM (10 cm^3), the organic layers

10   combined, dried over anhydrous magnesium sulphate, filtered and concentrated to a

yellow oil which was purified by column chromatography [petroleum ether 60-80 °C

: DCM 6 : 1 eluting to 4 : 1] to yield a glassy white solid.

Yield 0.57 g (80 %); (Found: C, 85.16; H, 9.40. requires C, 85.66; H, 9.06);

v_{max}(KBr)/cm^{-1} 3436, 2927, 1609, 1589, 1512, 1463, 1285, 1249, 1177, 826 *m/z*

15   [MALDI] 2425 (MH^+)

Figure 8:

G2-BX$_2$

The G2-BX$_2$ (**21**) was prepared as follows (see Figure 8).

20   *Tert*-butyl lithium (1.7 M, 0.4 cm^3, 0.644 mmol) was added to a cold (dry-ice/acetone

bath) solution of the aryl bromide **G2-Br**, prepared in Example 8, (454 mg, 0.403

mmol) in 3 cm^3 of anhydrous THF under argon atmosphere. The mixture was stirred

at -78 °C for 1.5 h. Tributyl borate (0.7 cm^3, 2.59 mmol) was added to the mixture

and the reaction was stirred at -78 °C for 1.5 h and then room temperature for further

25   3 h before being quenched with 3 M $HCl_{(aq)}$ (1 cm^3). The mixture was diluted with

water (2 cm^3) and ether (3 cm^3). The two layers were separated. The aqueous layer

was extracted with ether (3 x 4 cm^3). The organic layer and the ether extracts were

combined, washed with brine (1 x 8 cm^3) and dried over anhydrous magnesium

sulfate. The solvents were completely removed. Purification on silica gel column

30   using ethyl acetate-light petroleum (0:1 to 1:10) as eluent gave 376 mg (~86%) of **21**,

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where BX_2 represents a boron based functionality, where the $B(OBu)_2$ is partially hydrolysed, at its foci as a pale yellow oil; δ_H(200 MHz; $CDCl_3$) 0.83-1.02 (24 H, m, Me), 1.22-1.62 (32 H, m, CH_2), 1.65-1.83 (4 H, m, CH), 3.91 (8 H, m, $ArOCH_2$), 7.02 (8 H, m, ArH), 7.64 (8 H, m, ArH), 7.72-7.83 (6 H, m, ArH), and 8.02-8.12 (3

5   H, m, ArH).

Figure 6:

2,7-Bis(3,5-di{3,5-di[4-(2-ethylhexyloxy)phenyl]phen-1-yl}phen-1-yl)fluorene (22)

10   A mixture of the $G2-BX_2$ **(21)** (Figure 8) (148 mg, 0.136 mmol), 2,7-
dibromofluorene **(13)** (17 mg, 0.054 mmol), tetrakis(triphenylphosphine)palladium
(0) (5 mg, 4.3 ×

10^{-6} mol), aqueous sodium carbonate (2M, 0.2 cm^3), ethanol (0.2 cm^3) and toluene
(0.5 cm^3) was degassed and heated under reflux for 20 h under argon. The crude was

15   purified by column chromatography [silica gel, petroleum ether 40-60 °C eluting to
petroleum ether 40-60 °C : ethyl acetate 10 :1] to give an impure product which was
further purified by column chromatography [silica gel, petroleum ether 40-60 °C
eluting to petroleum ether 40-60 °C : ethyl acetate 30 : 1].

Yield 36.4 mg (30 %) δ_H(400 MHz; $CDCl_3$) 7.74-8.02 (m, 24 H), 7.65 (d, 16 H), 7.03

20   (d, 16 H), 4.13 (s, 2 H), 3.92 (d, 16 H), 1.77 (m, 8H), 1.25-1.60 (m, 64), 0.85-1.00
(m, 48 H), *m/z* [MALDI] 2255 (M^+). The $G2-Bx_2$ **(21)** was prepared as follows (see
Figure 8):

Example 15

25   This follows Figure 7.

2-Bromo-9,9-dihexylfluorene **(24)** 9,9,9',9'-Tetrahexyl-2,2'-bifluorenyl **(26)** and 7,7'-
Dibromo-9,9,9',9'-tetrahexyl-[2,2']bifluorenyl **(27)** can be obtained following Lee et
al, Thin Solid Films, 2000, <u>363</u>, 76 while 2-(9,9-Dihexylfluoren-2-yl)-4,4,5,5-
tetramethyl-1,3,2-dioxaborolane **(25)** can be obtained following Ranger et al,

30   Macromolecules, 1997, <u>30</u>, 7686.

7,7'-Bis-[4,4''-bis-(2-ethyl-hexyloxy)-[1,1';3',1'']terphenyl-5'-yl]-9,9,9',9'-tetrahexyl-[2,2']-bifluorenyl (28)

A mixture of compound **27** (150 mg, 1 82 x 10^{-4} mol), compound **12** (Figure 5) (279

5   mg, 4.55 x 10^{-4} mol), tetrakis(triphenylphosphine)palladium (0) (16 mg, 1.37 x 10^{-5}

mol) in aqueous sodium carbonate (2M 0.5 cm³), ethanol (0.5 cm³) and toluene (2

cm³) was heated under reflux for 24 h under argon. Dilute $HCl_{(aq)}$ (3M, 5 cm³) and

DCM (10 cm³) were added and the organic layer separated, washed with water (10

cm³), dried over anhydrous magnesium sulphate, filtered and concentrated to a brown

10   oil which was purified by column chromatography [silica gel, petroleum ether 40-60

˚C : DCM 4 : 1] to yield a white glassy solid.

Yield 124 mg (42%); (Found: C, 84.78; H, 9.56; requires C, 86.60; H, 9.49); δ_H(200

MHz; CDCl₃) 7.61-7.85 (m, 26 H) 7.04 (m, 8 H), 3.98 (d, 8 H), 2.10 (t, 4 H), 1.78 (m,

4 H), 0.72-1.60 (m, 78 H); v_{max}(KBr)/cm⁻¹ 2926, 1608, 1512, 1464, 1441, 1284, 1251,

15   1176, 1034, 815; m/z [MALDI] 1635 (M⁺)

2-(7-Bromo-9,9-dihexylfluoren-2-yl)-thiophene (29)

A mixture of 2,7-dibromo-9,9-dihexylfluorene (**7**) (8.0 g, 16 mmol), 2-

tributylstannylthiophene (2.98 g, 8.0 mmol), tetrakis(triphenylphosphine)palladium

20   (0) (200 mg, 1.73 x 10^{-4} mol) aqueous sodium carbonate (2M, 2 cm³), toluene (5 cm³)

and ethanol (2 cm³) was heated under reflux for 24 h under argon. Toluene and

ethanol were removed and hexane (10 cm³) and aqueous KI (2%, 10 cm³) added and

the mixture stirred vigorously for 1 h. Diethyl ether (10 cm³) and dilute $HCl_{(aq)}$ (3M,

10 cm³) were added, the aqueous layer separated and washed with diethyl ether (2 x

25   10 cm³). The organic layers were combined, dried over anhydrous magnesium

sulphate, filtered and concentrated to a dark brown oil which was purified by column

chromatography [silica gel, hexane] to yield a pale jade coloured oil.

Yield 2.23 g (56%); δ_H(200 MHz; CDCl₃) 7.08-7.75 (m, 9 H), 1.98 (m, 4 H), 1.10 (m,

12 H), 0.78 (t, 6 H), 0.65 (quint, 4 H); v_{max}(KBr)/cm⁻¹ 3435, 2856, 1456, 1377, 1062,

30   812, 694; m/z [APCI⁺] 496 (MH⁺), 417

-26-

2-Bromo-5-(7-bromo-9,9-dihexylfluoren-2-yl)-thiophene (30)

NBS (0.73 g, 4.11 x 10^{-3} mol, freshly recrystallised) was added slowly to a solution of 2-(7-Bromo-9,9-dihexylfluoren-2-yl)-thiophene (**29**) (1.85 g, 3.74 x 10^{-3} mol) in

5   chloroform (20 cm³) and glacial acetic acid (20 cm³) whilst heating under reflux. The solution was allowed to heat for a further 3 mins, cooled to RT and aqueous sodium metabisulphite solution (10 cm³) was added. The organic layer was separated, washed with water (2 x 10 cm³), aqueous sodium carbonate (2M, 2 x 10 cm³), water (2 x 10 cm³), dried over anhydrous magnesium sulphate, filtered and concentrated to a green oil.

10   Yield 2.08 g (97%) δ_H(200 MHz; CDCl₃) 7.42-7.72 (m, 6 H), 7.14 (d, 1 H), 7.08 (d, 1 H), 1.98 (m, 4 H), 1.10 (m, 12 H), 0.78 (t, 6 H), 0.68 (quint, 4 H); v_{max}(KBr)/cm⁻¹ 2954, 1599, 1456, 1245, 1062, 1005, 880, 814, 791

2-[4,4''-Bis-(2-ethyl-hexyloxy)-[1,1';3',1'']terphenyl-5'-yl]-5-{7-[4,4''-bis-(2-ethyl-

15   *hexyloxy)-[1,1';3',1'']terphenyl-5'-yl]-9,9-dihexyl-fluoren-2-yl}-thiophene (31)*

A mixture of compound **30** (200 mg, 3.48 ' 10^{-4} mol), compound **12** (Figure 5) (530 mg, 8.71 x 10^{-4} mol), tetrakis(triphenylphosphine)palladium (0) (30 mg, 2.6 x 10^{-5} mol), aqueous sodium carbonate (2M, 0.5 cm³), methanol (0.5 cm³) and toluene (2 cm³) was heated under reflux for 4 d under argon. Dilute $HCl_{(aq)}$ (3M, 10 cm³) and

20   DCM (10 cm³) were added, the organic layer separated, washed with water (100 cm³), dried over anhydrous magnesium sulphate, filtered, concentrated to a brown oil and purified by column chromatography [silica gel, DCM : hexane 1 : 4] to yield a green glassy solid.

Yield 220 mg, (46 %); (Found: C, 83.58; H, 9.52; S, 2.26 requires C, 84.05; H, 9.02; S,

25   2.31); δ_H(400 MHz; CDCl₃) 7.61-7.82 (m, 20 H), 7.45 (d, 1 H), 7.42 (d, 1 H), 7.04 (m, 8 H), 3.98 (d, 8 H), 2.10 (t, 4 H), 1.78 (m, 4 H), 0.72-1.60 (m, 78 H); v_{max}(KBr)/cm⁻¹ 2927, 1608, 1512, 1460, 1441, 1284, 1250, 1177, 1033, 825; *m/z* [MALDI] 1285 (M⁺)

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Example 16

Compound	Device structure	Peak efficiency (PE) (cd/A)	Voltage at PE	Brightness at PE (cd/m²)	Max brightness and voltage cd/m² at V	Turn on voltage (V)
10* Ex 12	ITO/PEDOT (50 nm)/10 (60 nm)/Ca (20 nm)/Al (100 nm)	0.09	33	24	24 at 33	20
10†	ITO/PEDOT (50 nm)/10 (80 nm)/Ca (20 nm)/Al (100 nm)	0.2	34	35	35 at 21	21
17 Ex 13	ITO/PEDOT (50 nm)/17 (100 nm)/Ca (20 nm)/Al (100 nm)	0.1	14	13	35 at 12	7.0
18 Ex 13	ITO/PEDOT (50 nm)/18 (100 nm)/Ca (20 nm)/Al (100 nm)	0.3	9.0	15	55 at 12	7.0
20 Ex 14	ITO/PEDOT (50 nm)/20 (100 nm)/Ca (20 nm)/Al (100 nm)	0.1	21	13	34 at 23	12.8
28 Ex 15	ITO/PEDOT (50 nm)/28 (100 nm)/Ca (20 nm)/Al (100 nm)	0.1	9.0	65	130 at 12	5.0
28	ITO/PEDOT (50 nm)/PVK (30 nm)/28 (80 nm)/Ca (20 nm)/Al (100 nm)	0.3	8.0	100	335 at 11	4.0
31 Ex 15	ITO/PEDOT (50 nm)/31 (100 nm)/Ca (20 nm)/Al (100 nm)	0.3	9.0	135	460 at 12	5.0
31	ITO/PEDOT (50 nm)/PVK (30 nm)/31 (80 nm)/Ca (20 nm)/Al (100 nm)	1.1	7.0	127	1905 at 10	3.8
28 & 31	ITO/PEDOT (50 nm)/PVK (30 nm)/28:31 (50:50 wt%) (80 nm)/Ca (20 nm)/Al (100 nm)	0.94	8.4	265	3100 at 12	3.8

-28-

The devices tested above were prepared as follows:

1. Etch ITO squares 12x12 mm into 4x12 mm ITO strip by acid etch

2. Acetone rinse for 10 minutes with ultrasonication

3. Propan-2-ol rinse for 10 minutes with ultrasonication

4. Substrates dried under dry nitrogen flow

5. Substrates subject to oxygen plasma treatment for 5 minutes at 100 W

6. PEDOT spun from water solution at 2500 rpm for 1 minute

7. PEDOT layer dried in air at 85 °C for 5 minutes

8. Dendrimer film deposited by spin coating

9. Substrates placed in vacuum evaporator

10. 20 nm of calcium deposited at 0.1 nm/s under vacuum of $1x10^{-6}$ mBar

11. 100 nm of aluminium deposited at 0.1 nm/s under vacuum of $1x10^{-6}$ mBar

Preparation of a PVK layer

1. PVK solution prepared 6 mg/ml in amylene stabilised CHCl3

2. Films spun onto ITO cleaned as previously described at 4000 rpm for 1 min

3. Films dried at 65 °C in nitrogen atmosphere for 20 minutes

4. Films allowed to cool

5. Top dendrimer layer spin coated from toluene

For **10*** the dendrimer was spin-coated from chloroform whilst for **10†**
tetrahydrofuran was used.

The approximate CIE coordinates of the EL emission from a neat layer of **31** are
x=0.16, y=0.2, from a neat layer of **28** are x=0.17, y=0.09, and from a blend of **31**
and **28** are x=0.16, y=0.11.

Devices made with a neat layer of dendrimer 31 (fluorene-thiophene core) are more
efficient than those made with a neat layer of 28 (bifluorene core) but the color is

-29-

blue-green rather than deep blue. hence it can be advantageous to blend the

dendrimers, as the device using mixture of **28** and **31** has both a deep blue color and

a good efficiency. The use of a hole-transporting layer (PVK) can improve the

efficiency and lower the turn on voltage of the devices.

-30-

CLAIMS

1.   A light-emitting device incorporating as its light emitting element at least one
compound having the formula (I):

5   CORE-[DENDRITE(-Q)$_a$]$_n$ (I)

in which the CORE represents an atom or group, n represents an integer of at least 1, Q
is a proton or a surface group, a is an integer and DENDRITE, which may be the
same or different if n is greater than 1, represents a conjugated dendritic structure
comprising aryl and/or heteroaryl groups connected to each other via bonds between

10   sp^2 hybridised ring atoms of said aryl or heteroaryl groups, CORE terminating in the
first single bond which is connected to an sp^2 hybridised ring atom of an (hetero)aryl
group to which more than one conjugated dendritic branch is attached, said atom
forming part of the DENDRITE, the CORE and/or DENDRITE being luminescent;
provided that the compound is not

15

wherein each Z is a group of formula:

-31-

$$\text{---}\langle\text{benzene ring}\rangle\text{---O-CH}_2\text{-CH(C}_2\text{H}_5\text{)(C}_4\text{H}_9\text{)}$$
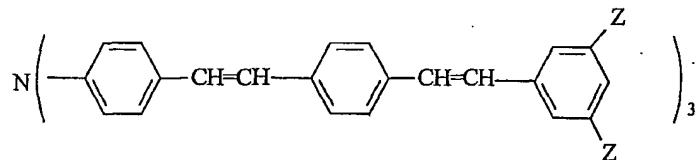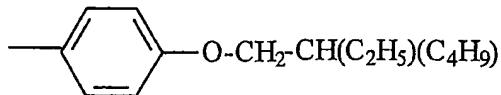
2.   A light emitting device incorporating as its light emitting element a compound having the formula (II):

CORE-[DENDRITE(-Q)$_a$]$_n$ (II)

in which the CORE represents an atom or group other than a nitrogen atom or a group of
5   tetrahedral shape, n represents an integer of at least 1, Q is a proton or a surface group, a is an integer and DENDRITE, which may be the same or different if n is greater than 1, represents a conjugated dendritic structure comprising aryl and/or heteroaryl groups connected to each other via bonds between sp^2 hybridised ring atoms of said aryl or heteroaryl groups, CORE terminating in the first single bond
10   which is connected to an sp^2 hybridised ring atom of an (hetero) aryl group to which more than one conjugated dendritic branch is attached, said atom forming part of the DENDRITE, the CORE and/or DENDRITE being luminescent.

3.   A device according to claim 1 or 2 wherein at least one DENDRITE represents a conjugated dendritic structure comprising aryl and/or heteroaryl groups
15   connected to each other via bonds between sp^2 hybridised ring carbon atoms of said aryl or heteroaryl groups.

4.   A device according to any one of claims 1 to 3 wherein at least one dendron contains a phenyl branching group linked directly to at least one aryl branching group which is not phenyl.

-32-

5.   A device according to one of claims 1 to 3 wherein at least one dendron contains a phenyl branching group linked to one or more phenyl branching groups via an aryl linker.

6.   A device according to any one of the preceding claims wherein the said light-emitting element is deposited by solution processing.

7.   A device according to any one of the preceding claims wherein the distal aryl groups of the DENDRITES of the light emitting element are substituted by one or more Q which are surface groups and which may be the same or different.

8.   A device according to any one of the preceding claims wherein the HOMO-LUMO energy gap of the light emitting element decreases from the distal aryl groups to the CORE.

9.   A device according to any one of the preceding claims wherein the CORE of the light emitting element is not luminescent.

10.   A device according to any one of the preceding claims wherein the CORE of the light emitting element is not luminescent and the HOMO-LUMO energy gap of the DENDRITE decreases from the distal aryl groups to the attachment point to the CORE.

11.   A device according to any one of the preceding claims wherein the said light emitting element is prepared by a convergent route.

12.   A device according to any one of the preceding claims which comprises a layer of said light emitting element together with one or more layers of other materials, preferably including a hole-transporting or electron transporting layer.

13.   A device according to any one of the preceding claims which is a light emitting diode (LED).

14.   A device according to any one of the preceding claims wherein the dendrimer is blended with another dendrimer and/or polymer and/or molecular compound.

-33-

15.   A device according to any one of the preceding claims in which at least one
Q is a surface group selected from branched and unbranched alkyl (especially t-
butyl), branched and unbranched alkoxy, hydroxy, alkylsilane, carboxy, carbalkoxy,
and vinyl; a further-reactable alkene, (meth)acrylate, sulphur-containing, or silicon-
containing group; a sulphonyl group; a polyether group; a C_1 to C_{15} alkyl (preferably
t-butyl) group; an amine group; a mono-, di- or tri-C_1 to C_{15} alkyl amine group; a
-COOR group wherein R is hydrogen or C_1 to C_{15} alkyl; an -OR group wherein R is
hydrogen, aryl, or C_1 to C_{15} alkyl or alkenyl; an -O_2SR group wherein R is C_1 to C_{15}
alkyl or alkenyl; an -SR group wherein R is aryl, or C_1 to C_{15} alkyl or alkenyl; an
-SiR_3 group wherein the R groups are the same or different and are hydrogen, C_1 to
C_{15} alkyl or alkenyl, or -SR' group (R' is aryl or C_1 to C_{15} alkyl or alkenyl), aryl, and
heteroaryl

16.   A device according to any one of the preceding claims wherein CORE is
selected from one or more moieties of benzene, pyridine, pyrimidine, triazine,
thiophene, fluorene, divinylbenzene, distyrylethylene, divinylpyridine, pyrimidine,
triazine, divinylthiophene, oxadiazole, coronene, or a fluorescent dye or marker
compound or a metallic element such as a lanthanide, or iridium complex, or a
metalloporphyrin.

17.   A method of manufacturing a light emitting device comprising the steps of
providing a film of at least one compound as defined in claim 1 or 2 and, optionally,
one or more other films to provide a laminate, adhering to one surface of the said
film or laminate a substantially transparent electrode (preferably ITO), and
depositing on the other surface of the said film or laminate a metallic cathode,
preferably selected from Al, Mg/Ag, and Ca.

18.   A film formed of a compound as defined in claim 1 or 2, preferably of
thickness from 20 to 200 nanometres, more preferably 50 to 150 nanometres.

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19.   A colour display device including pixels comprising one or more light emitting devices as claimed in any one of claims 1 to 15.

20.   A colour display device according to claim 18 wherein a substantially white or neutral background is provided by one or more of said compounds which inherently emit such a background colour.

5

21.   Use of a compound as defined in claim 1 or 2 in any semiconducting device other than a light emitting device, for example, a photodiode, solar cell, FET, or solid state triode.

Figure 1

A General Method for the Preparation of Higher Generation Dendritic Intermediates
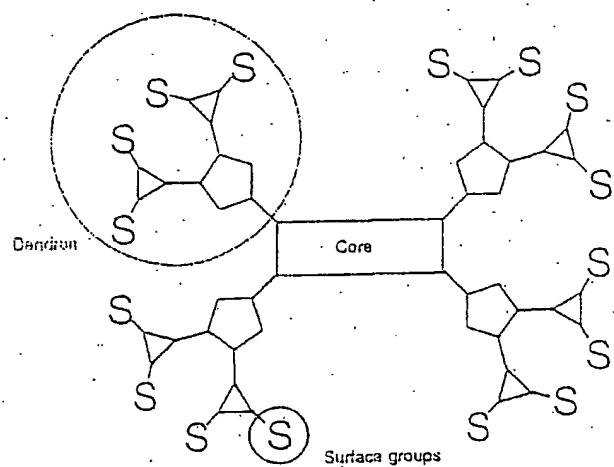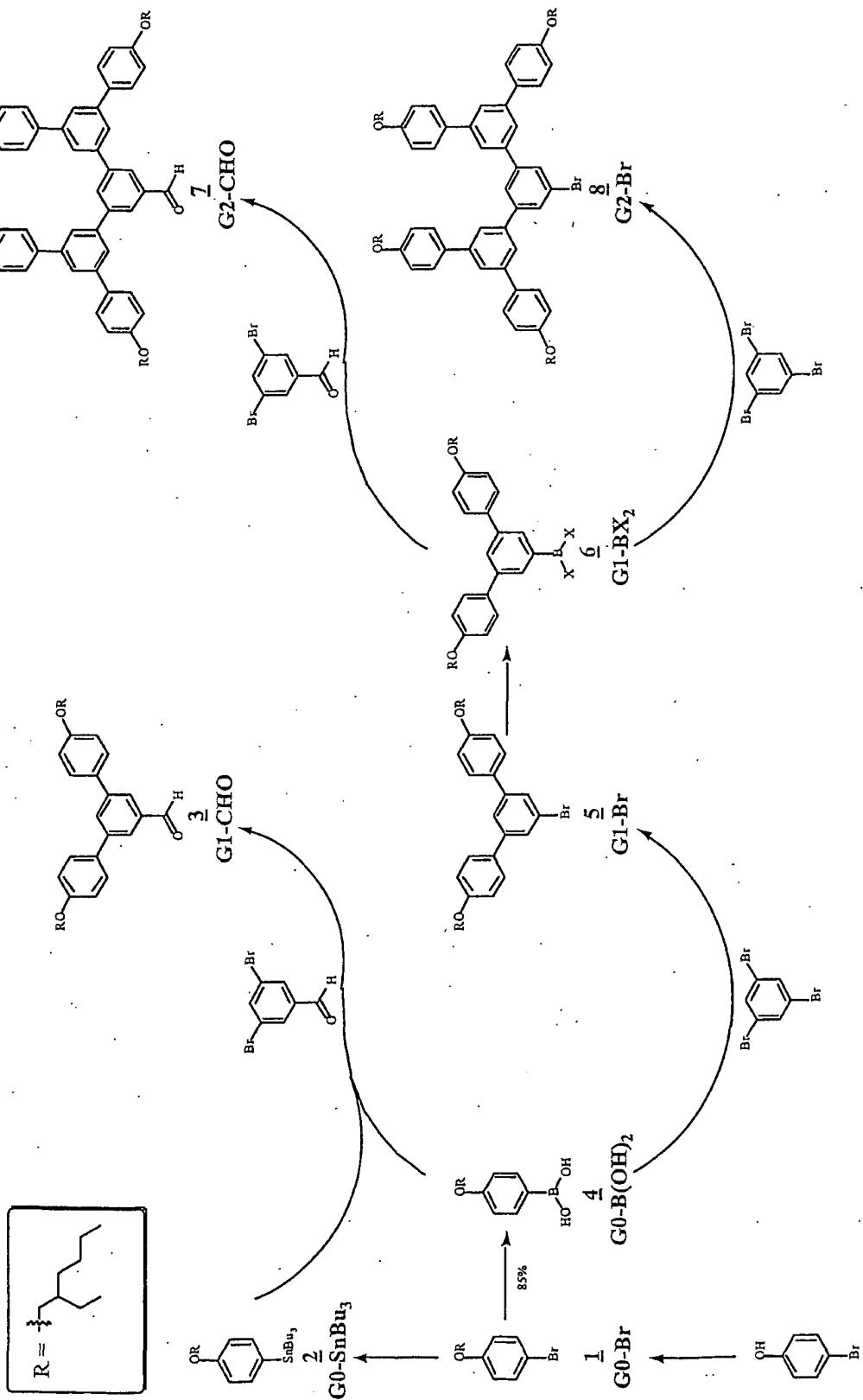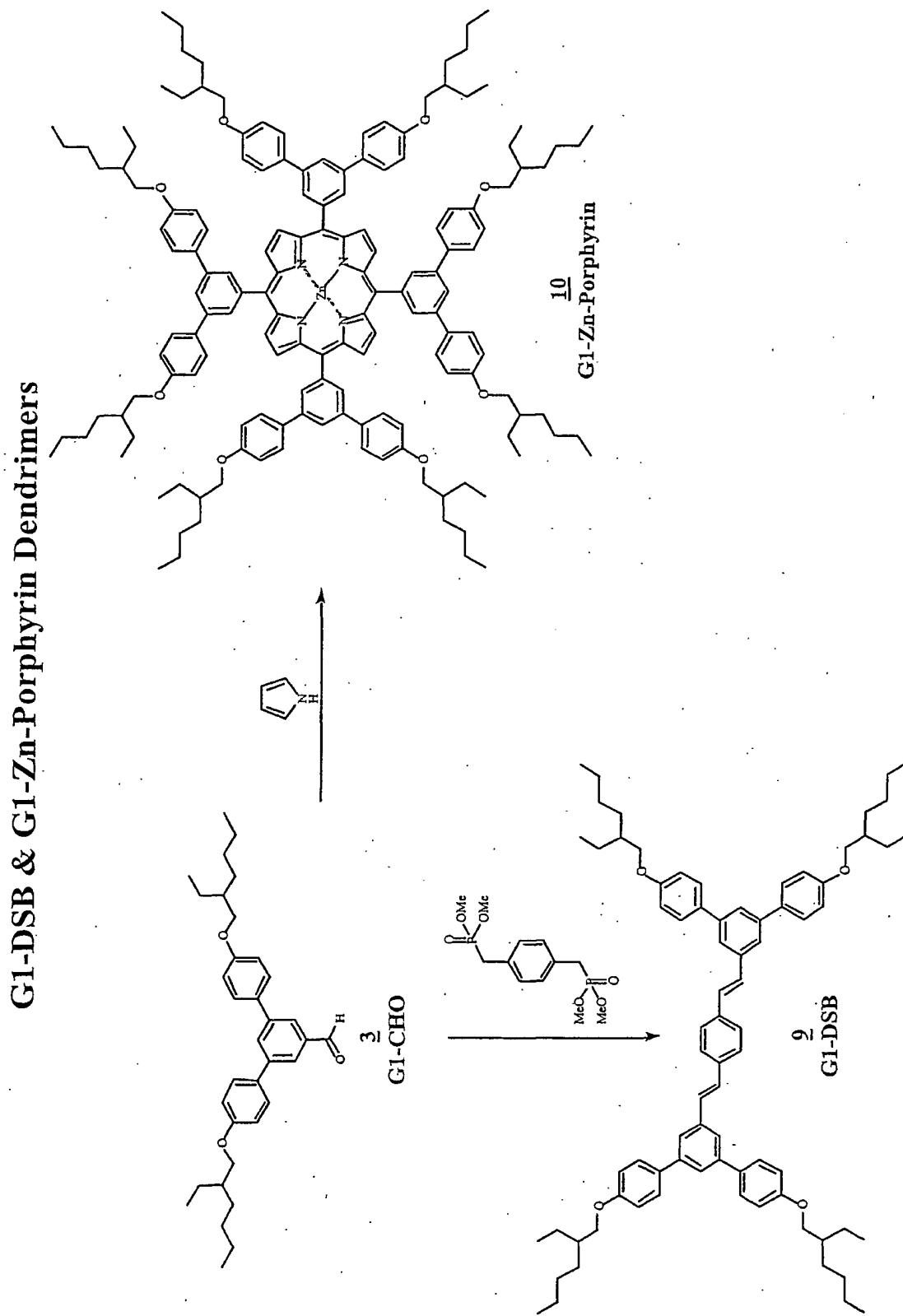
Figure 2

G1-DSB & G1-Zn-Porphyrin Dendrimers
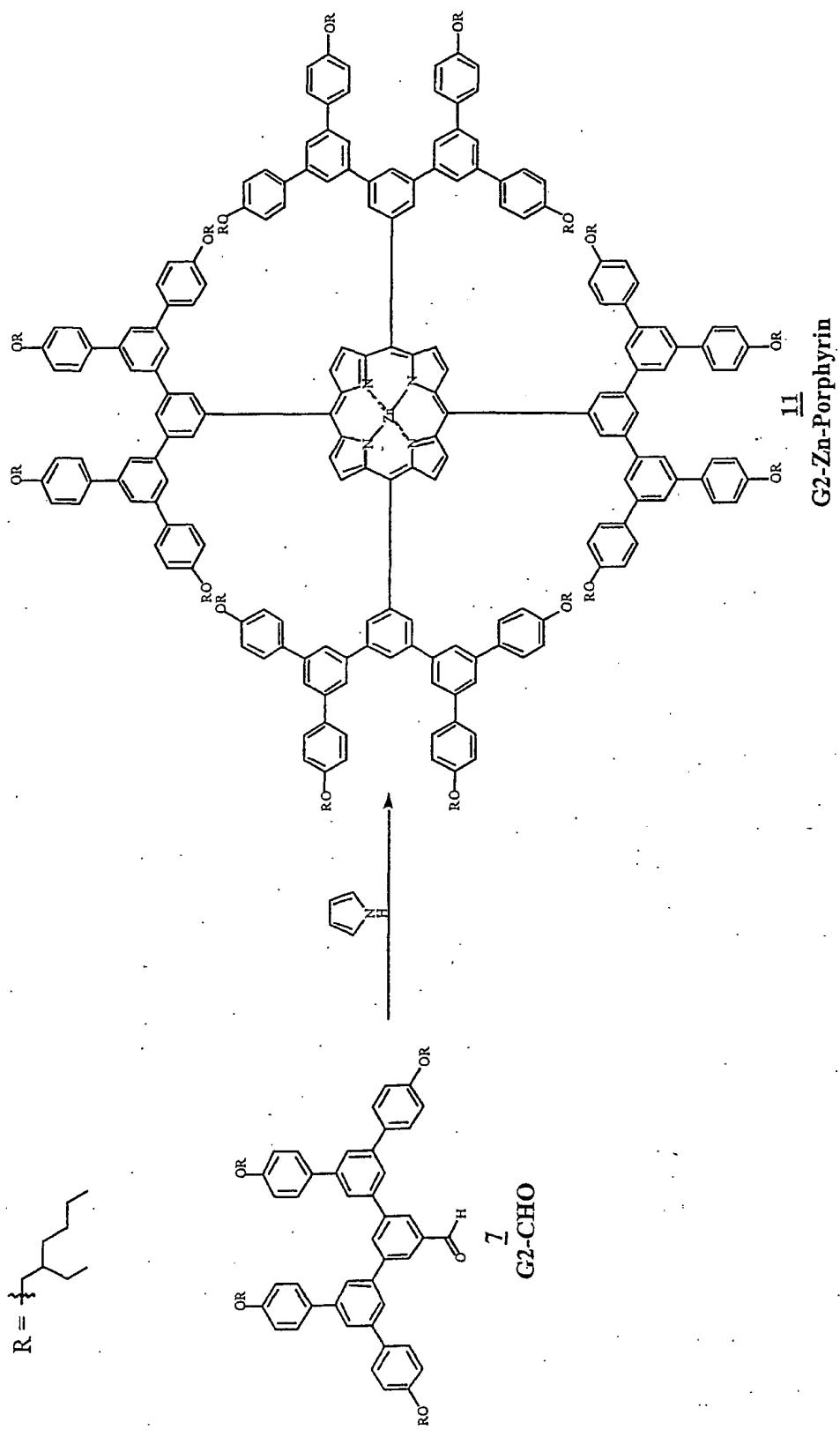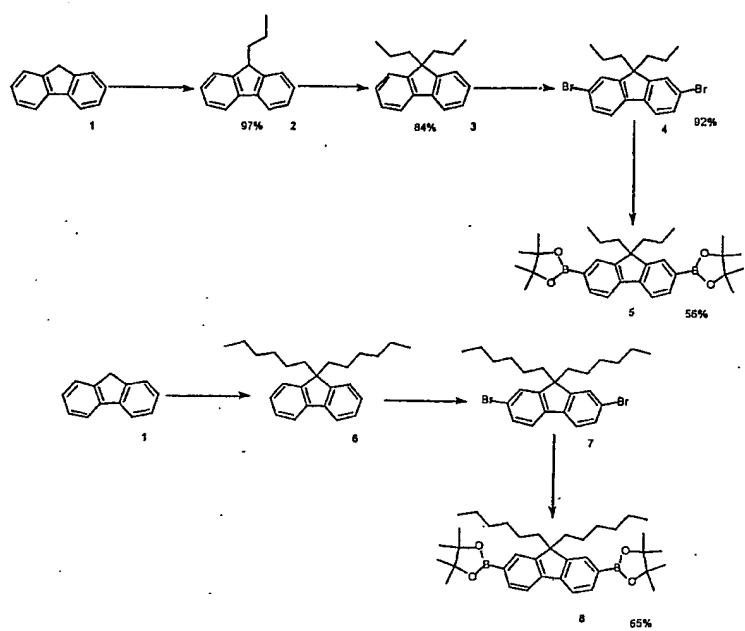
Figure 3
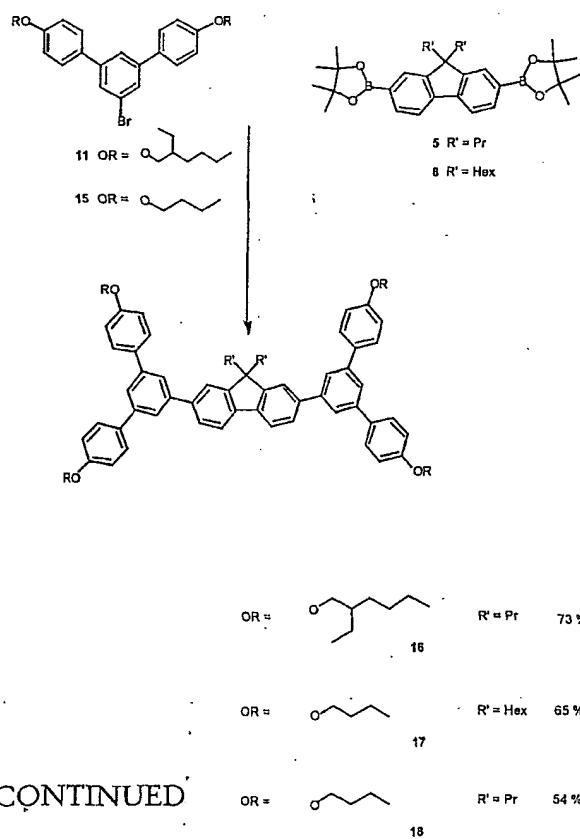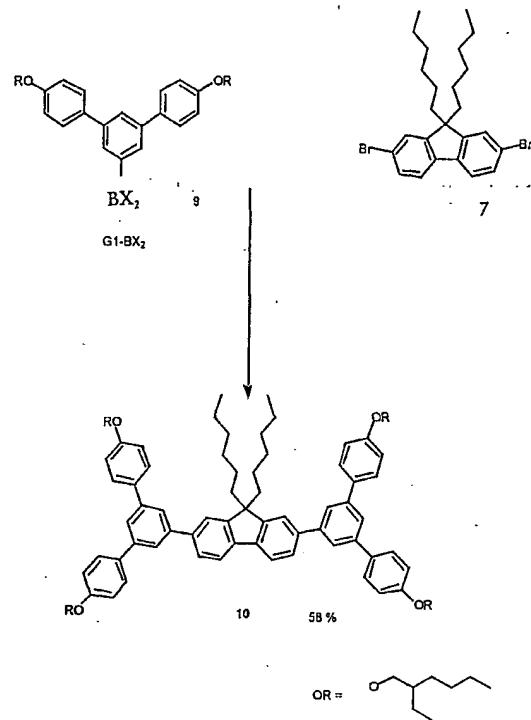
Figure 4

FIGURE 5

FIGURE 5 CONTINUED
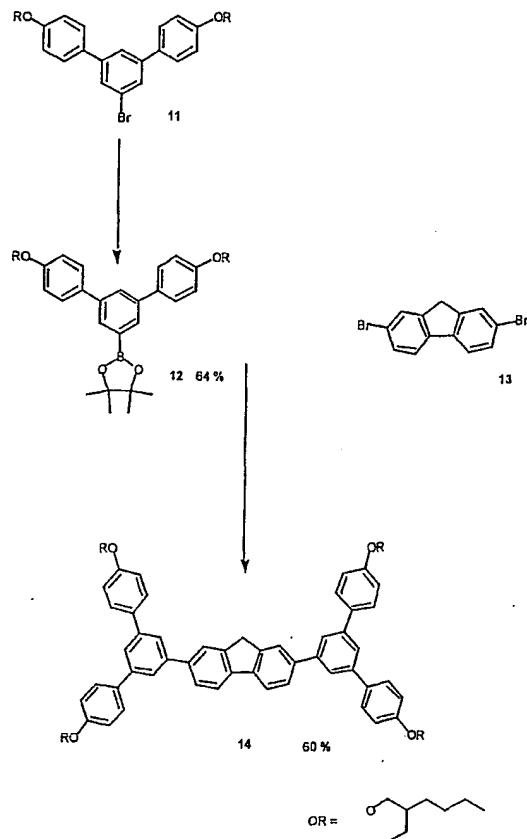
FIGURE 5 CONTINUED

FIGURE 6

BX₂   21

13

29 %
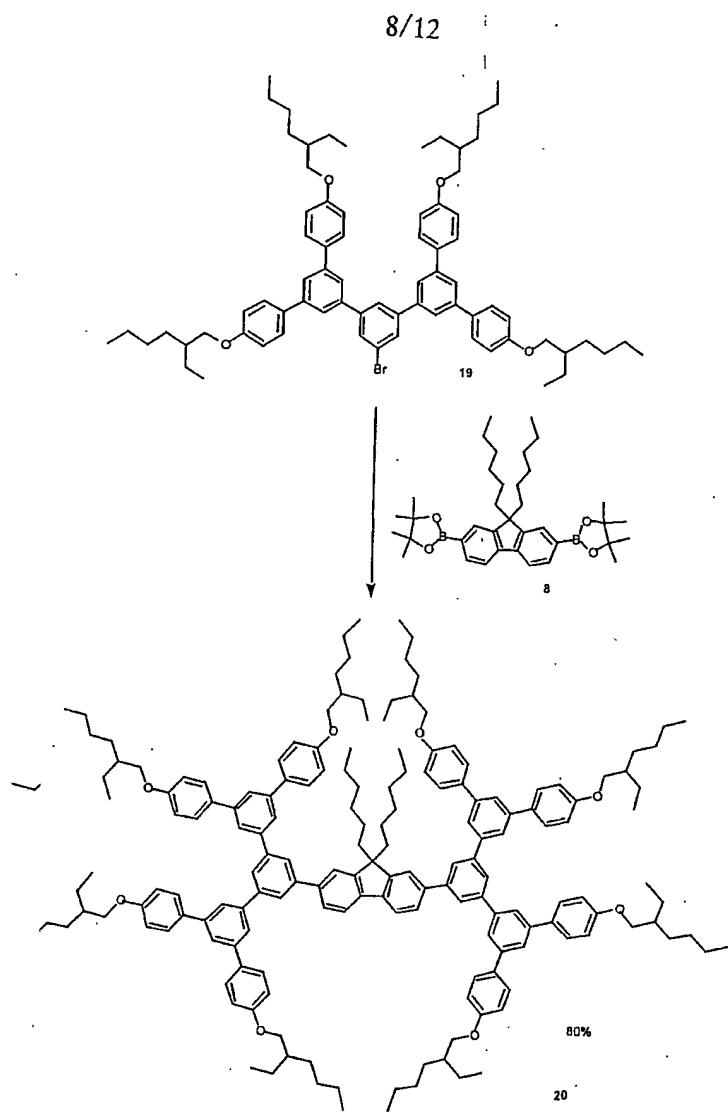
22
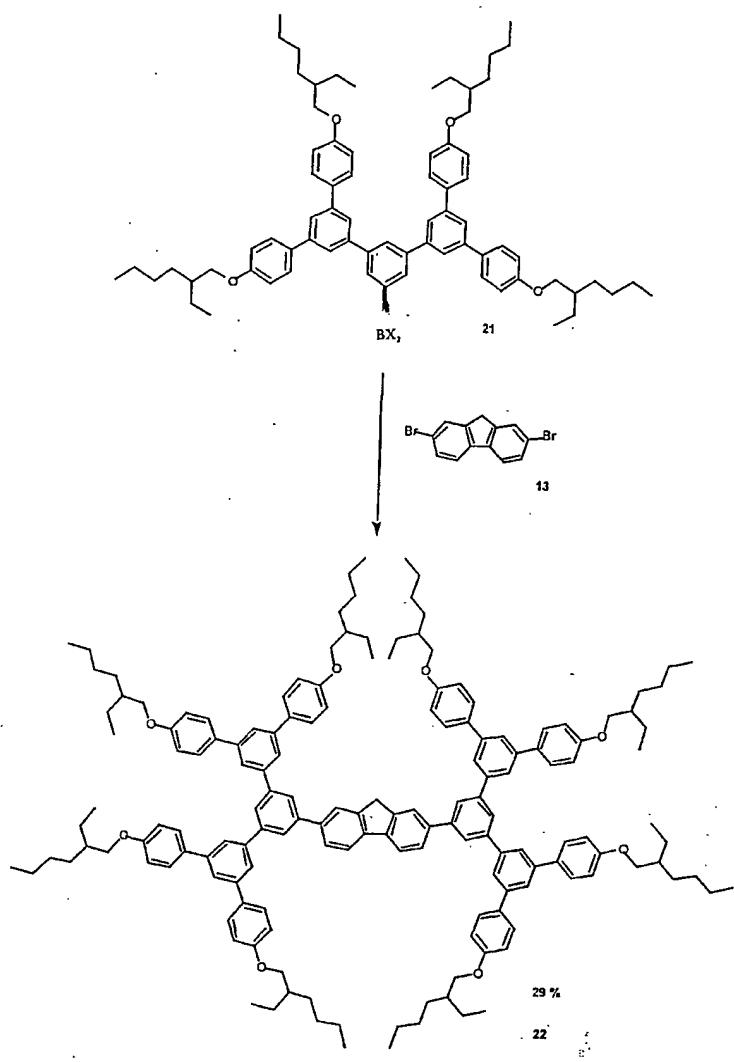
FIGURE 6 CONTINUED
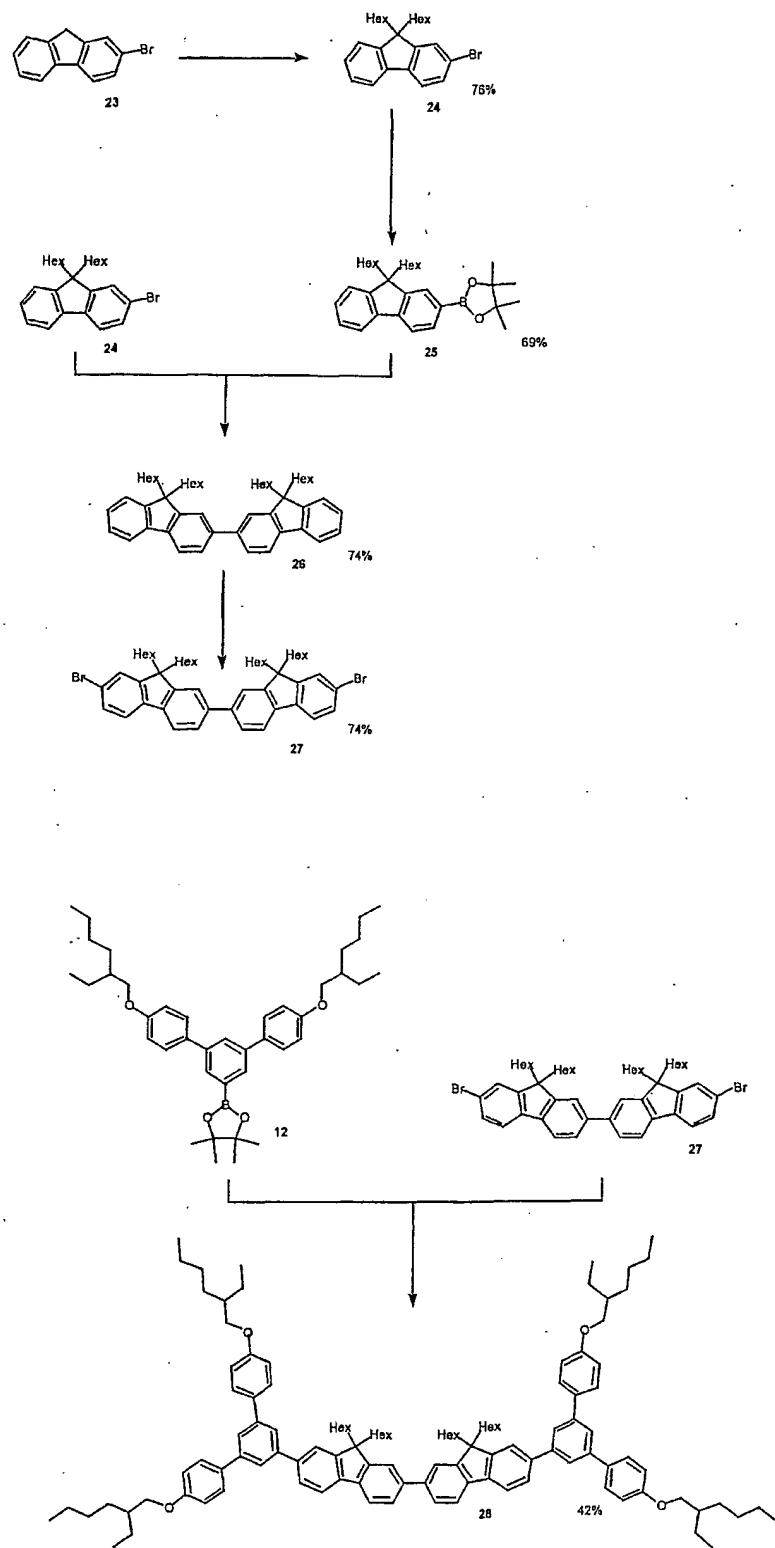
FIGURE 7
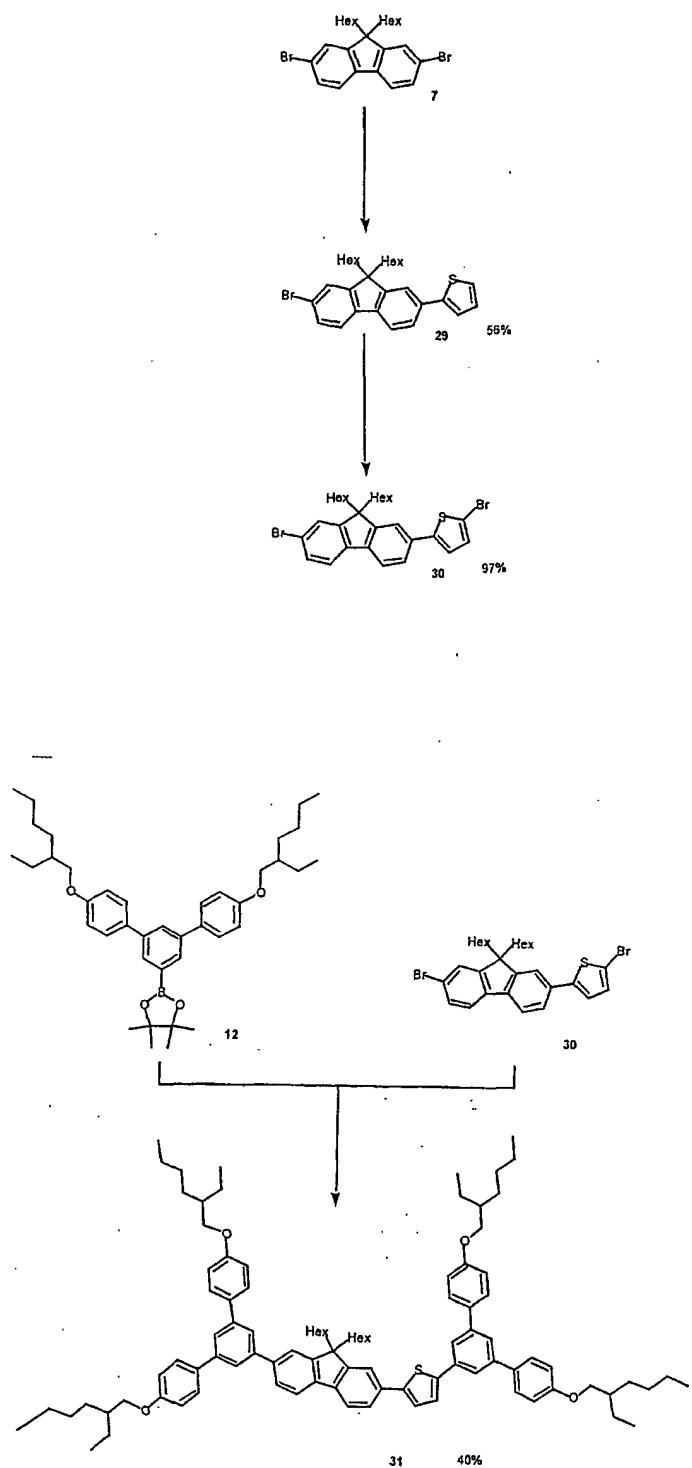
FIGURE 7 CONTINUED

$$\underline{33}$$
G0-Br

$$\underline{33}$$
G0-BOR₂

$$\underline{15}$$
G1-Br

$$\underline{21}$$
G2-BX₂
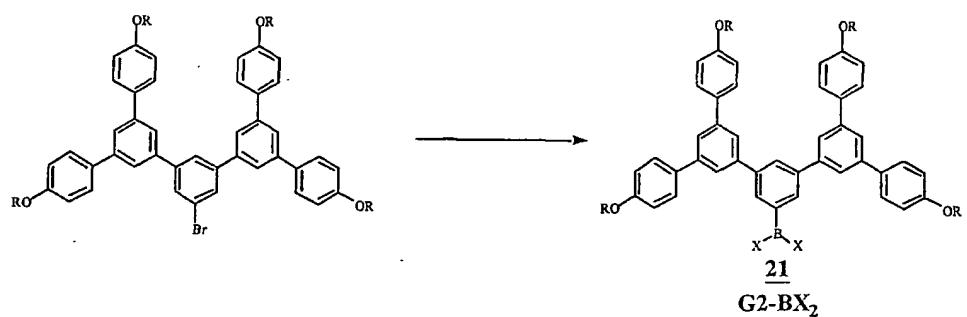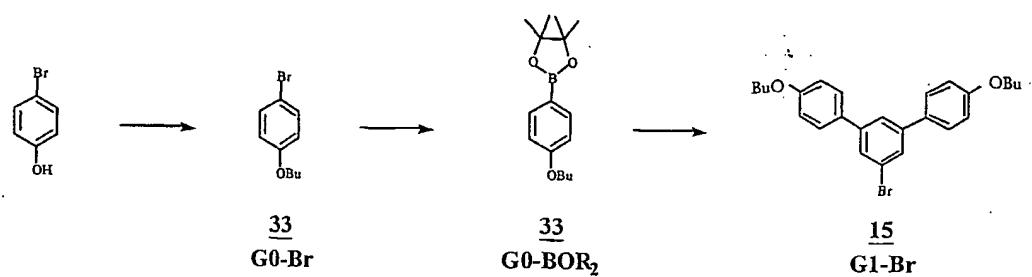
FIGURE 8

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   H01L51/30   C08G83/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7   H01L   C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, INSPEC, PAJ, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	S. SETAYESH, A. C. GRIMSDALE, T. J. WEIL, V. ENKELMANN, K. MÜLLEN, F. MEGHDALI, E. J. W: LIST, G. LEISING: "Polyfluorenes with Polyphenylene DEndron Side Chains: Toward Non-Aggregating, Light-Emitting Polymers" J. AM. CHEM. SOC., vol. 123, no. 5, 16 January 2001 (2001-01-16), pages 946-953, XP002199675 figure 4 --- -/--	1-5,16

| X | Further documents are listed in the continuation of box C. | | X | Patent family members are listed in annex. |

° Special categories of cited documents:

'A' document defining the general state of the art which is not considered to be of particular relevance

'E' earlier document but published on or after the international filing date

'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

'O' document referring to an oral disclosure, use, exhibition or other means

'P' document published prior to the international filing date but later than the priority date claimed

'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

'&' document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 May 2002	04/06/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Königstein, C

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	KIMURA M ET AL: "Energy transfer within ruthenium-cored rigid metallodendrimers" TETRAHEDRON LETTERS, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 41, no. 35, August 2000 (2000-08), pages 6809-6813, XP004213954 ISSN: 0040-4039 the whole document	1-3,7,8, 11,15,16
X	WO 99 21935 A (SAMUEL IFOR DAVID WILLIAM ;HALIM MOUNIR (GB); ISIS INNOVATION (GB)) 6 May 1999 (1999-05-06) cited in the application the whole document	1,2, 17-21
P,X	LUPTON J M ET AL: "CONTROL OF ELECTROPHOSPHORESCENCE IN CONJUGATED DENDRIMER LIGHT-EMITTING DIODES" ADVANCED FUNCTIONAL MATERIALS, WILEY INTERSCIENCES, WIENHEIM, DE, vol. 4, no. 11, August 2001 (2001-08), pages 287-294, XP001072704 ISSN: 1616-301X figures 1B,1C	1,2,9,10
A	WANG P-W ET AL: "ELECTROLUMINESCENT DIODES FROM A SINGLE-COMPONENT EMITTING LAYER OF DENDRITIC MACROMOLECULES" ADVANCED MATERIALS, VCH VERLAGSGESELLSCHAFT, WEINHEIM, DE, vol. 8, no. 3, 1 March 1996 (1996-03-01), pages 237-241, XP000558253 ISSN: 0935-9648 the whole document	

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Information on patent family members

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			CN	1277624 T	20-12-2000
			EP	1027398 A1	16-08-2000
			WO	9921935 A1	06-05-1999
			JP	2001521053 T	06-11-2001